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EDITOR: S. N. ROYE

Junior Editors: BENOY K. BANERJEE & S. A. KULKARNI

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EDITOR'S NOTE

It has been decided to publish in **TECHNOLOGY** research papers from scientists and technologists outside FCI Ltd. provided these are:

- (i) original and related to science and technology.
- (ii) approved by external referees chosen by the Editor, and
- (iii) communicated from reputed institutions and written by workers with adequate experience.

Papers for publication in **TECHNOLOGY** are, therefore, welcome. These should be sent in duplicate (complete with illustrations and abstracts) to the Editor. Books, reports, proceedings of symposia, conferences, etc., meant of review in this journal, are welcome.

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The pore structures of alumina, silica, Florisil and of their thermal and salt modifications have been investigated by the technique of high resolution electron microscopy. It has been proposed and found substantially correct that the widening of pores is due to the growth of globules by absorbent modifications. No significant increase in globule diameter was, however, noticed in the sintered alumina and silica, but globule swelling was found to be 8-fold with sintered Florisil, 5 to 6-fold with coppersulphate treated silica and alumina, 2 to 3-fold with sodium-sulphate modified silica and alumina. The degree of agglomeration of the globules, their defects, size, shape and distribution, mode of packing characteristics, and the chemical nature of modifying salts and absorbents are the important variables which govern the details of three dimensional pore architecture.

A great need was felt for further research to understand the forces working behind clustering of globules and the relationships of globules with parameters of pore. It has been observed that practically any change in pore geometry is reflected in the gas-solid chromatographic behaviour of these adsorbents. Hence, identification and correlation of pore parameters with GSC-properties will constitute an important breakthrough not only in gas chromatography, but also in all other uses of adsorbents. In other words, GSC has all the potentials to emerge as a very fast and convenient technique for studying the structure of porous materials including supported catalysts.

Electron Microscopic Studies of the Pore Structure of Some Adsorbents and Their Modifications for Evaluation of Gas-Solid Chromatographic Properties

By P. C. BANERJE*, SAMIR K. GHOSH AND N. C. SAHA,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

In earlier publications^{1,2} Saha *et al* have demonstrated a drastic alteration in the pore structure of adsorbents, such as silica, alumina and Florisil, when these are first coated with transition metals and other salts and then fired at high temperatures. It has also been pointed out that any change in pore geometry is reflected in gas-solid chromatographic properties when these adsorbents are used as column materials. Most suitable sorbent molecules for studying pore geometry are the saturated hydrocarbons, particularly the normal alkanes, since their retentive mechanism is entirely governed by the parameters of pore. The primary object of this work is to recommend gas-solid chromatography as a powerful technique for investigating into the details of pore architecture. Perhaps, the lack of theoretical knowledge and sufficiently powerful experimental techniques for a detailed understanding of pore structure did not stimulate the

much needed research in unravelling the precise role of pore geometry in gas chromatography.

Swelling and agglomeration of the existing primary globules have been proposed by the present authors as a probable mechanism of pore widening and other textural changes of adsorbents by salt and thermal modification. The degree of crystallinity, size distribution, peripheral shape and roughness and mode of packing of the globules determine the details of three dimensional pore architecture of adsorbents. The conventional data of surface area, pore volume and pore size distribution cannot at all explain the above properties. Ottenstein³, Kiselev *et al*⁴⁻⁶ and Janak and Staszewski⁷ have applied the powerful technique of electron microscopy for studying the pore structure of supports and adsorbents commonly used in gas chromatography.

In this work high resolution electron microscopy has been applied on a few GSC adsorbents and their physical and chemical modifications in order to supplement

* Present address: Central Scientific Instrument Organisation, Chandigarh.

the information on pore structure obtained by the conventional methods; the ultimate object being the correlation of these pore parameters with GSC properties. It has been realised that more refined and powerful experimental techniques are needed to elucidate such parameters as length, tapering, tortuosity, constrictions and mode of interlinking of the pores. Proper understanding of the functioning of adsorbents in fields other than gas chromatography, will also result from this type of investigation.

Experimental

The methods of modification of the samples of silica alumina and Florisil (Hewlett-Packard) were described in earlier papers^{1,2}. Particle size, 30/60 mesh, of the starting samples was reduced further in an agate mortar until they made fairly stable suspensions in amyl alcohol. A drop of this suspension was placed on a specimen grid, previously coated with a carbon supporting film, and the alcohol was allowed to evaporate. The grids were examined in a Siemens Elmiskop-IA Electron Microscope operated at 80 Kv. Only the representative structures in the specimen were photographed with a maximum magnification of 120,000. The distribution of pore and globule sizes from the electron microphotos was based on counting the number of pores or globules having a given diameter varying within $\pm 2.5\text{\AA}$.

Results

Electron micrographs of silica and its four modifications were given in Fig. 1, of alumina along with its four modified forms in Fig. 2 and of Florisil with its two modifications in Fig. 3.

Pore volume, surface area and average pore diameter (from BET method) of these adsorbents were given in Table 1 along with pore size distributions derived from the electron microphotographs. The distribution of globular sizes in some of the adsorbents were given in Table 2. The average pore and globule diameters were compared in Table 3.

Discussion

The gas chromatographic properties such as, retention volume, heat of adsorption, peak symmetry, power of elution, selectivity, resolution and speed of analysis of all the adsorbents mentioned in this work were discussed in detail in two earlier publications^{1,2}. The adsorbates were chosen from the saturated hydrocarbons, especially the normal alkanes.

A wide variation in retention behaviour was noted in

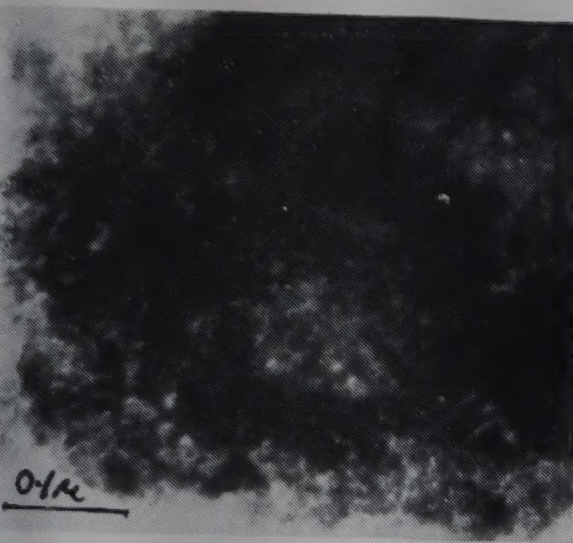
these adsorbents, which also exhibited corresponding difference in pore geometry. Indications are there that two adsorbents of different chemical composition having similar pore geometry will have similar gas-solid chromatographic properties for the normal paraffins. Of course, it is a thing of remote future to identify and isolate quantitatively the precise contribution of each and every parameter of pore towards retention properties.

Silica Gel Adsorbents: The electron micrograph of ordinary silica in Fig. 1A reveals its complete amorphous nature and highly microporous structure with interconnected pores. The pores range from 10 to 50Å with 50 per cent having 37Å and the mean globule diameter is 80Å. It is noted from electron microphoto that the ratio of average pore to globule diameter is 0.44. A range of values (0.6 to 2.3) for this ratio has been reported by Kiselev⁶ for a number of silica gels. Obviously, this ratio is determined by the variables of gel preparation. Mention may be made that the silica gel used in this work did not elute even methane at 175°C.

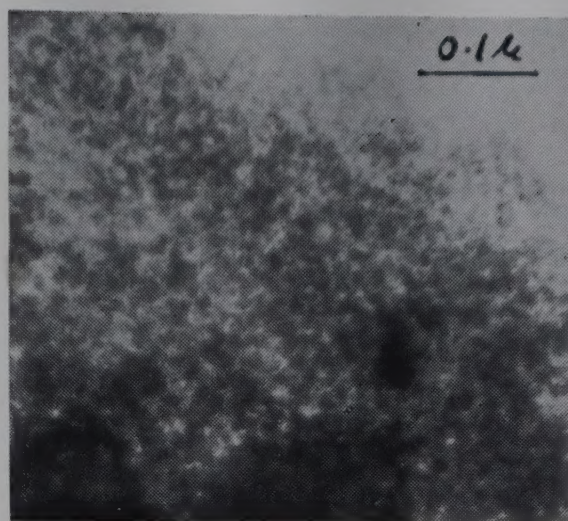
Sintering of the same silica at 950°C has caused a big change in the pore spectrum (Fig. 1B) by widening 72 per cent of the pores to 50Å and above (vide Table 1). The globules and pore network are much more distinct in Fig. 1B than in the starting silica gel. Not much difference in globule size distribution can be noticed in Figs. 1(A and B). Of course, an accurate determination of globule size distribution for untreated and sintered silica will need electron micrographs of considerably higher resolution. The decrease in surface area with simultaneous increase in elution capacity of the heated silica is indicative of pore widening.

There is a significant variation in the degree of interlinking of pores, which is more prominent in the starting and heated silicas; but the pores seem to be rather more isolated in the salt treated silicas in Figs. 1C and 1D. The complexity in the intersecting pore network has increased to a great extent the effective pore lengths (i.e. the diffusion/desorption paths) in the untreated and heated silicas compared to the salt-modified silicas of corresponding pore spectrum. This is reflected in much longer elution times in the former adsorbents than in the latter.

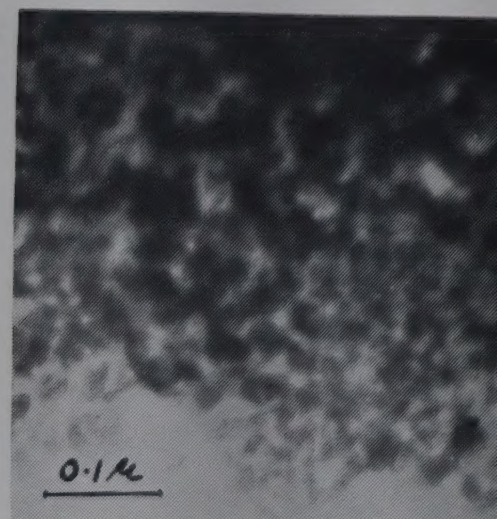
The major sintering reaction i.e. dehydroxylation involving two or more elementary corpuscles did not proceed enough in Figs. 1A and 1B to give rise to distinct and bigger globules which are noticed in the salt modified silicas in Figs. 1(C, D & E). This positive role of the modifying salts cannot be clearly understood unless the



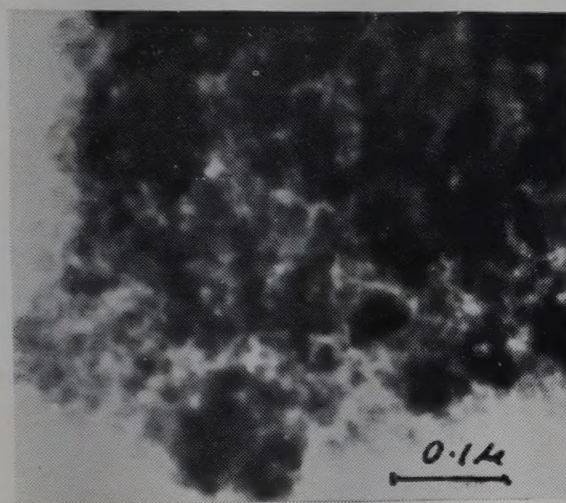
1A. Initial Silica Gel



1B. After Sintering at 950°C

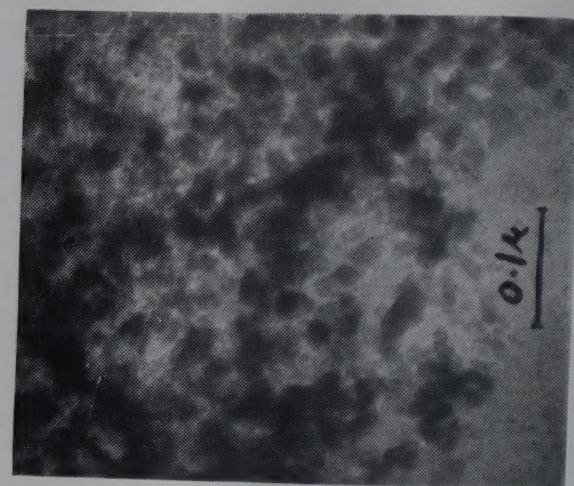


1C. After Coating with Copper Sulphate
Followed by Heating to 950°C

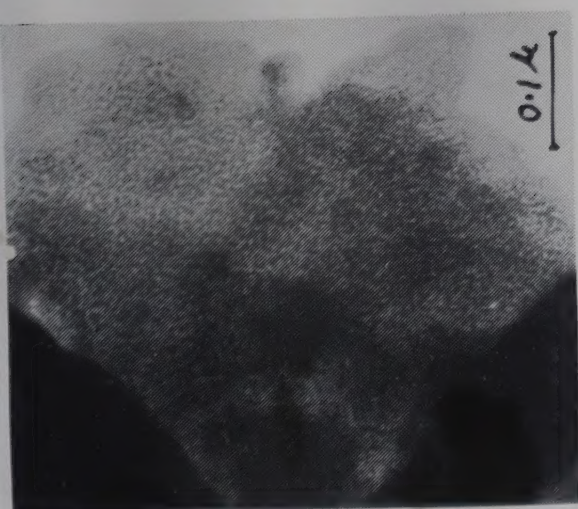


1D. After Thermal Treatment with Copper
Ammonium Sulphate

Fig. 1—Electron Micrographs of Adsorbents from Silica Gel. [The black surface is material of the support; the white dots are free spaces.]

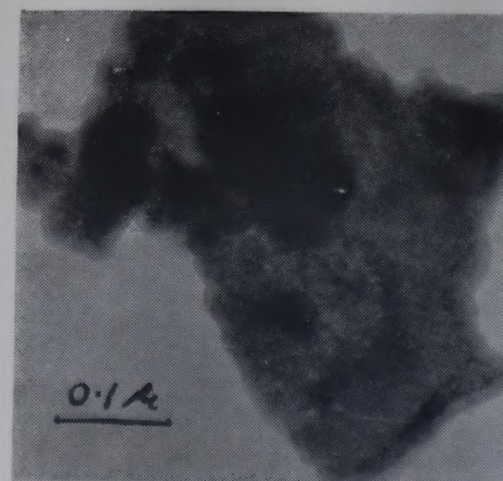


1E. After Thermal Treatment with
Sodium Sulphate

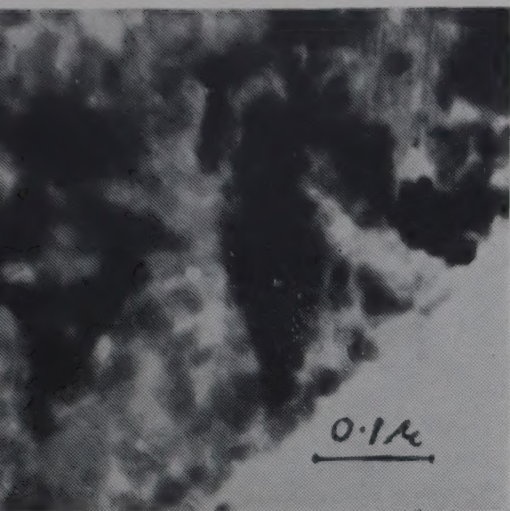


2A. Initial Alumina Gel

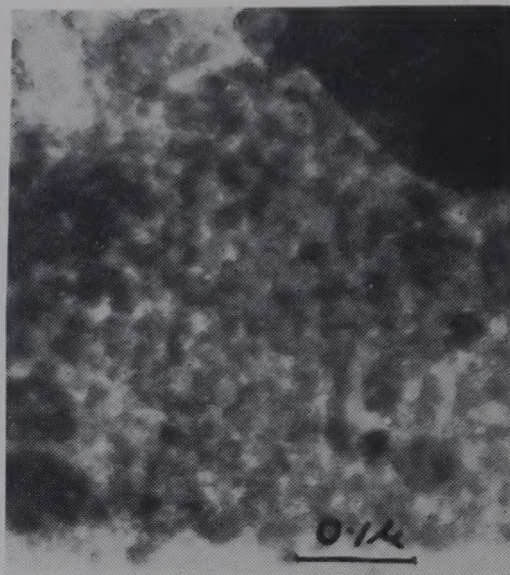
Fig. 2—Electron Micrographs of Alumina and its Modifications. [The black surface is material of the support; the white dots are pores.]



2B. After Calcining Alone at 950°C



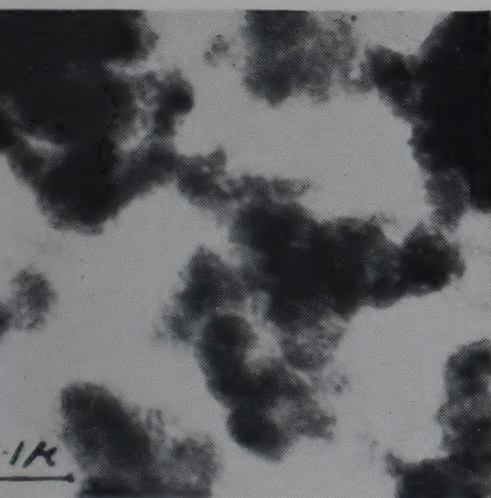
2C. After Copper Sulphate and Heat Treatments



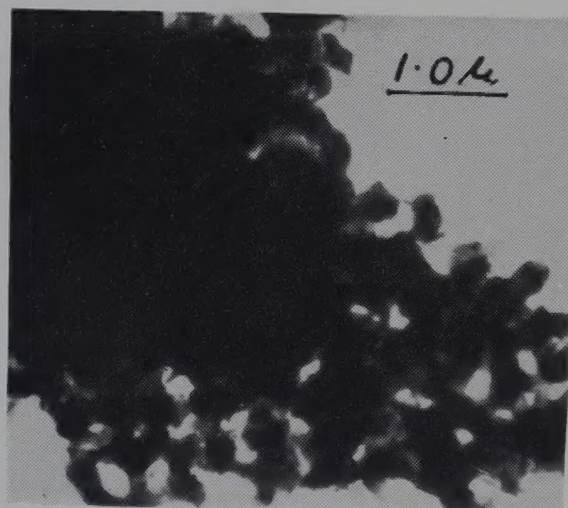
2D. After Thermal Treatment with Copper Sulphate



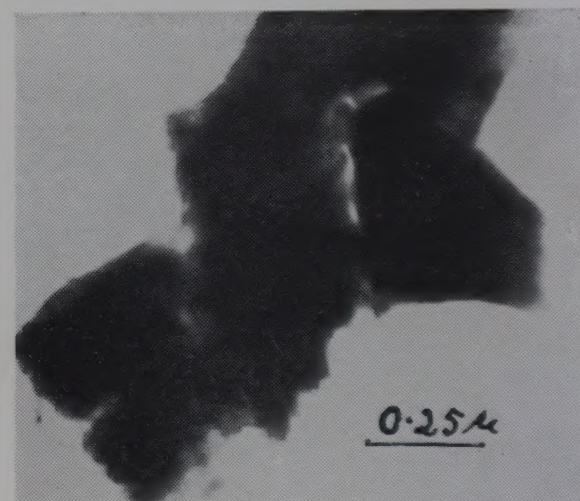
2E. After Thermal Treatment with Sodium Sulphate



3A. Initial Florisil



3B. Sintered Florisil



3C. Florisil Heated with Copper Sulphate

Fig. 3—Electron Micrographs of Florisil and its Modifications. [The black surface is material of the support; the white dots are free spaces.]

mode of chemical combination or otherwise of their remnants and their physical distribution are known. The size, shape and defects on the globules and their geometrical packing patterns have contributed to many subtle differences in the pore geometry of the modified adsorbents. The nature of binding forces working behind the clustering of the discrete globules could not be ascertained in this work. No definite proof of the formation of copper silicate glass (to act as cementing materials for

swelling and clustering of globules) could be observed in the microphotos. The openings on globules due to crystal defects have been differentiated in this paper as micropores from the macropores originating in the inter-globular voids. Comparison of the distribution of pore and globule sizes (in Tables 1 and 2) as well as the wide range of ratios of mean pore to globule diameters (in Table 3) reveal big difference in the packing geometry of globules for the adsorbents dealt in this work.

TABLE 1—SURFACE AREA AND AVERAGE PORE DIAMETER BY B.E.T. METHOD AND PORE SIZE DISTRIBUTION BY ELECTRON MICROSCOPIC TECHNIQUE OF SOME COMMON ADSORBENTS AND THEIR THERMAL AND SALT MODIFICATION

Adsorbents	Electron Microscopic Method														
	B.E.T. Method		Percentage of Pores with Median Diameter in Å												
	Surface area, m ² /g.	Pore dia. Å	25	37	50	75	100	125	150	200	250	300	350	400	500
Silica gel*	375.0	25	12	50	16	—	—	—	—	—	—	—	—	—	—
Silica ge, heated	296.0	36	18	—	74	7	1	—	—	—	—	—	—	—	—
SiO ₂ -Cu (NH ₃) ₄ SO ₄ , heated	29.0	194	—	—	—	8	68	14	10	—	—	—	—	—	—
SiO ₂ -CuSO ₄ , heated	24.0	398	—	—	—	—	—	—	—	35	19	39	—	4	3
SiO ₂ -Na ₂ SO ₄ **	1.5	1640	—	—	—	—	10	—	17	21	20	4	12	—	8
Al ₂ O ₃	152	32	3	10	87	—	—	—	—	—	—	—	—	—	—
Al ₂ O ₃ , heated	44	133	1	—	6	40	20	31	2	—	—	—	—	—	—
Al ₂ O ₃ -Cu (NH ₃) ₄ SO ₄	11.4	511	—	—	1	1	76	2	16	4	—	—	—	—	—
Al ₂ O ₃ -CuSO ₄ , heated***	7.2	761	—	—	—	—	—	—	—	—	—	—	—	—	—
Al ₂ O ₃ -Na ₂ SO ₄	42.0	81	—	—	55	36	9	—	—	—	—	—	—	—	—
Florisil	191	62	100	—	—	—	—	—	—	—	—	—	—	—	—
Florisil, heated****	1.5	5240	—	—	—	—	—	—	—	—	—	—	—	—	—
Florisil-CuSO ₄ , heated	Nil	Nil	—No pores visible—												

* 10Å—1%, 20Å—12%, 30Å—8%, 40Å—1%

** 600—875Å—7%, 450Å—1%

*** 66Å—1%, 93Å—9%, 132Å—31%, 166Å—56%, 199Å—3%

**** 1000Å—12%, 1500Å—30%, 2000Å—36%, 2500Å—12Å, 3000Å—10%

TABLE 2—DISTRIBUTION OF GLOBULE SIZE IN DIFFERENT ADSORBENTS

Adsorbents	% of Globules with Median Diameter, Å									
	83	125	166	208	250	290	333	375	417	500
SiO ₂ -CuSO ₄ , heated	—	—	4	—	20	8	40	8	20	—
SiO ₂ -Cu(NH ₃) ₄ SO ₄	—	—	20	—	32	4	28	—	4	12
SiO ₂ -Na ₂ SO ₄ , heated	42	—	18	—	20	2	12	—	6	—
Al ₂ O ₃ -CuSO ₄	—	—	25	—	63	—	6	—	6	—
Al ₂ O ₃ -Cu(NH ₃) ₄ SO ₄	4	4	20	20	48	—	4	—	—	—
Al ₂ O ₃ -Na ₂ SO ₄	40	38	22	—	—	—	—	—	—	—
Florisil-CuSO ₄ *heated	—	—	—	—	—	—	—	—	—	—
Florisil **	—	—	—	—	—	—	—	—	—	—
Florisil, heated ***	—	—	—	—	—	—	—	—	—	—

* 16000Å—25%, 17000Å—25%, 20000Å—25%, 45000Å—25%

** 415Å—50%, 498Å—50%

*** 3000Å—50%, 3980Å—50%

TABLE 3—COMPARISON OF MEAN PORE AND GLOBULE DIAMETER OF DIFFERENT ADSORBENTS

Adsorbents	Electron Microscopic Diameters of		Ratio of Pore to Globule Diameter
	Pore Å	Globule Å	
Silica gel	35	80	0.44
Silica gel, heated	70	85	0.82
Alumina	48	40	1.20
Alumina, heated	100	45	2.22
Florisil	25	456	0.06
Florisil, heated	1890	3486	0.51
SiO ₂ -Cu(NH ₃) ₄ SO ₄ , heated	106	395	0.27
SiO ₂ -CuSO ₄ , heated	234	326	0.72
SiO ₂ -Na ₂ SO ₄ , heated	237	205	1.16
Al ₂ O ₃ -Cu(NH ₃) ₄ SO ₄ , heated	106	216	0.49
Al ₂ O ₃ -CuSO ₄ , heated	149	244	0.61
Al ₂ O ₃ -Na ₂ SO ₄ , heated	63	122	0.52

The electron micrograph in Fig. 1C of the copper-sulphate treated silica shows very distinct globules which are completely free from micropores on the surface. Most of the globules are spheroidal in shape with smooth surface. The globules vary in size from 166 to 417Å. A globule is found to be interlinked with 3 to 5 others to form a colony, generating a pore spectrum of 200 to 500 Å. Hence, copper sulphate has brought about a drastic change in the pore geometry of silica gel accompanied by equally big alterations in GSC properties. For example, copper-sulphate modified silica gives fastest elution for a given hydrocarbon among all the adsorbents studied.

Copper-ammonium sulphate treated silica (Fig. 1D) also reveals similar distinctive features. But the globules have diffuse and rough outlines, most of them are defective crystals with intraglobular micropores. All these factors add up to explain the existence of comparatively smaller pores and larger surface area in the complex copper-salt treated silica than in the simple copper-salt treated silica. The globule cluster is not sharp enough to permit accurate counting of members in contact with each other. Although Fig. 1D shows more of bigger globules with average diameter of 395Å compared with the corresponding value of 326Å in Fig. 1C, the geometry of packing of rough and wedged corpuscles did not favour creation of pores bigger than 150Å in the former adsorbent, while in the latter all the pores are larger than 200Å, more uniform and less spread in size.

The electron micrograph (Fig. 1E) of the silica treated

with sodium-sulphate shows distinct globules with rough surface. A remarkable feature in the globule spectra of Fig. 1E is the presence of about 50 per cent of the corpuscles with 83Å in diameter, which is absent in Figs. 1C and 1D. Many of the inter-globular pores are covered with sodium-silicate glass. Nevertheless, the pore spectrum is fairly wide, ranging from 100 to 800Å. The average pore diameter of 1640Å obtained by the B.E.T. method cannot be explained from the micrograph in Fig. 1E. Considering the pore size distribution (Table 1) the surface area of 1.5 m²/g. for this adsorbent also appears to be too low. Judging from the pore structure, sodium-sulphate treated silica (pore volume² 0.123 ml/g. surface area 1.5 m²/g. mean pore diameter 1640Å) was expected to give faster elution than copper-sulphate modified silica (pore volume 0.477 ml/g. surface area 24 m²/g. mean pore opening 398 Å from electron microscope), but in actual practice the former showed about 1.5 times slower elution of a given hydrocarbon. The cause might be the presence of constriction, tortuosity or too much cross-linking in the pore network of the sodium salt treated silica.

Alumina Adsorbents: Electron micrograph of ordinary alumina in Fig. 2A shows a uniform microporous structure with 87 per cent of the pores having 50Å diameter, which is reflected in its smaller surface area and greater elution power compared with the control silica in Table 1. Moreover, the globules and pores appear to be more prominent in alumina than in silica. Sintered alumina has lost its original uniformity of pore geometry; only 7 per cent of the pores retained original size, and more than 90 per cent being enlarged to more than 50Å in diameter (Table 1). Hence, a much stronger sintering of alumina with large reduction in surface area compared to silica can be understood. Widening of pores in both the sintered alumina and silica is not accompanied by swelling of globules (Table 3) unlike the case with salt-modification. A probable mechanism is the comparatively loose packing geometry of the globules caused by sintering, so that the members in the globule cluster of the sintered adsorbents are more distended to generate larger interstices.

Copper-sulphate modification of alumina has generated an entirely different shape of corpuscles, namely, hexagonal with a new pattern of packing characteristics giving rise to small pores all of which are not circular in cross-section. A most distinctive feature of this electron micrograph in Fig. 2C is the existence of a few big channels of dimension 1000Å × 150-200Å bounded by crystal stacks. This might explain the high mean pore diameter of 761Å obtained by the B.E.T. method (Table 1). These

big channels were not considered in the pore size analysis by electron microscope. The globules are perfectly crystalline with distinct outlines and smooth surfaces.

It is noted from Fig. 2D that copper ammonium sulphate is a much poorer mineralizer than copper sulphate for the growth of alumina crystals. The globules are not hexagonal but are rather spheroids, with profuse crystal defects and vague outlines. The pores are nearly circular in cross-section. Smaller average pore diameter and somewhat smaller size of globules with rough and wedged surface explain the higher retentivity in GSC and reduced surface area of the complex copper-salt treated alumina compared with the copper-sulphate treated one. A general similarity can be observed in the electron microphotographs of the copper ammonium-sulphate modified alumina and silica, both having the same mean pore size of 216 and 244Å respectively.

A comparison of the electron micrographs in Figs. 2E and 1E with respect to size, shape and distribution of pores and globules reveals a very different effect of sodium-sulphate on the pore structure of alumina and silica. In alumina the surface is reduced from 152m²/g. to only 42m²/g. compared with 375m²/g. to 1.5m²/g. for silica. In alumina, variation in the distribution of globules is from 83 to 166Å and in pores from 50 to 100Å, the corresponding changes in silica are 100 to 500Å and 83 to 417Å. Sodium sulphate-treated alumina shows many globules with rough and diffuse periphery, whilst its silica counterpart shows a few big pore channels. In conformity with pore structure sodium-sulphate alumina adsorbent gives corrected specific retention volumes² (in ml/g. at 100°C) of 0.64 and 1.05 for normal butane and pentane respectively, the corresponding data for the other adsorbent are 0.15 and 0.19.

It is very probable that a modifying salt will cause more widening of pores and swelling of globules in silica than in alumina of equivalent pore structure. Therefore, the former adsorbent is more amenable to pore structure modification for faster elution of high molecular weight compounds.

Florisil Adsorbents: The electron micrograph in Fig. 3A of Florisil—a coprecipitate of silica and magnesia—shows distinct circular pore mouths with uniform diameter of 25Å. A vast majority of the pores are intra-globular, the inter-globular voids are not clearly visible. It is unclear why the B.E.T. method gives a high mean pore diameter of 62Å. The defective globules are spherical, ranging in size from 415Å to 498Å.

By sintering at 950°C the globules were lumped together to form a big particle with macropores of 0.1 to

0.3 micron (vide Fig. 3B). The original micropores were all eliminated and hence the surface area was reduced drastically. The pores seem to be isolated with no interconnections. This electron micrograph may be compared with Fig. 1 of Celite reported by Janak *et al*⁷.

This absorbent did not show any retention for hydrocarbons (upto C₂₀ being tested). The intertness and macroporous structure of this heated Florisil clearly indicate its suitability as a GLC support. Copper sulphate modification was expected to further enlarge the pores noticed upon sintering, but the almost completely fused mass of Florisil (vide Fig. 3C) did not show any surface area or pores, save and except a few cracks, thereby, rendering this material useless for GSC or GLC work. A search for a suitable modifying salt to control the sintering of Florisil for generation of pore structure comparable to that of either Chromosorb P or Chromosorb W is being continued.

Conclusion

Observations made in this work amply demonstrate the feasibility of alteration and control of pore structure of common adsorbents. Increase in mean pore diameter was about 25 times for alumina-copper-sulphate, 60 times for silica-sodium sulphate and 85 times for Florisil-heated. Maximum growth in globule size obtained was 4-fold for silica and 8-fold for alumina. Kiselev⁸ obtained about 20 times increase in globule diameter for silica by hydrothermal treatment. Hence, there is a considerable scope for further research on salt-thermal modification to achieve tailor-made adsorbents with average pore diameters of the order of say 100 to 1000Å for GSC and of a few microns for GLC.

A suggested implication of this work is relevant to the use of supported catalysts in industry. Heating of such a catalyst during use is likely to cause some change on the pore geometry of support (like alumina and silica) with foreign active catalyst materials embedded on its surface. The altered pore structure will affect properties of adsorption, desorption, diffusion of the reactants and products and their approachability towards the active catalyst material, the seat of which may also undergo subtle dislocation and consequent loss of activity. Therefore, the variables of thermal aging of the supported catalysts as well as the compatibility of the nature of support and active catalyst principle should be such as to give irreversible change in the pore geometry.

Acknowledgements

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The dependence of the rate of water gas shift reaction on the surface area of a few commercial Fe_2O_3 - Cr_2O_3 catalysts has been investigated. Although the activity of the catalysts expressed as the first order rate constant has been found to depend on the surface area of the reduced catalyst no quantitative relationship could be established. This is due to the fact that the activity of the catalyst depends on other factors besides surface area, such as composition, method of preparation, etc.

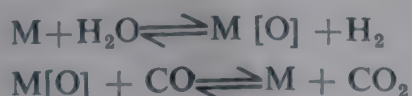
Dependence of Water Gas Shift Reaction Rate on Catalytic Surface

By G. SENGUPTA, N. RAY, S. P. SEN,

*Planning & Development Division,
Fertilizer Corporation of India Ltd, Sindri, Bihar*

The role of catalyst surface in determining the kinetics and path of a heterogeneous reaction is well-known. The magnitude of the activation energy for the catalytic reaction, i.e. the catalyst activity, is determined by the nature of adsorption and distribution of adsorbed molecules which in turn depends upon the surface properties of the catalyst.

In case of Fe_2O_3 - Cr_2O_3 type catalyst used for water gas shift reaction, several studies have been made to find out the influence of surface upon the reaction rate. It has been shown that during reaction the catalyst surface undergoes alternate oxidation-reduction¹⁻⁴.



The actual state of the active phase is determined by the oxidation potential of the reacting system which is given by

$$P_{\text{O}_2} = \frac{1}{K_{\text{H}_2\text{O}} K_{\text{CO}_2}} \left[\frac{P_{\text{H}_2\text{O}}}{P_{\text{CO}}} \frac{P_{\text{CO}_2}}{P_{\text{H}_2}} \right]$$

where P_{O_2} = oxidation potential of the system, expressed as the partial pressure of oxygen.

It is obvious, therefore, that the thermodynamic property of the catalyst surface during reaction should have an important effect on the catalyst activity. Therefore, any measurable property of the catalyst which can be related to the thermodynamic property of the active surface can give an idea about the activity of the catalyst.

Further investigations carried out by Kato² reveal that active spots which are thermodynamically very susceptible to reduction exist on the catalyst surface during reaction and the concentration and thermodynamic property of such active spots determine the extent of the reaction. If it is assumed that for a given set of reaction condition the thermodynamic property and the number of active spots per unit area of surface is same for all Fe₂O₃-Cr₂O₃ catalysts irrespective of their method of preparation, it can be concluded that the activity of the catalysts will depend upon the number of active spots available for reaction or, in other words, the activity will be proportional to the surface area of the catalyst. The present investigation was carried out to determine the extent of this dependence and to see if a quantitative relationship can be evaluated. Such relationship will obviously be very useful in the development of commercial catalysts.

Experimental

The catalysts used for this investigation were of commercial type. The original samples in the form of cylindrical pellets were crushed and sieved to obtain granules of -14 + 16 mesh (BSS) size. The reduction of the catalyst and its activity measurements were carried out in an all-glass system (Fig. 1).

About 1 g. of the catalyst diluted with about 4 g. of pyrex chips of -14 + 16 mesh was used. The height and the diam. of the catalyst bed were 4.5 and 1.2 cm respectively. The temperature of the reactor furnace was controlled by means of a temperature-controller. The reactor temperature was measured by means of a chromel-alumel thermocouple. The temperature difference between the top and the bottom of the catalyst bed was never more than 2°C.

The reduction was carried out at 450°C in a current of steam and gas mixture containing about 5 per cent carbon monoxide, 55 per cent hydrogen, 15 per cent

carbondioxide and rest nitrogen. At the initial stage one mole per cent of the reducing gas was dosed in a current of steam. The gas flow was gradually increased to 5 l./hr. and steam flow adjusted to give steam/gas ratio of 3. The activity measurements were carried out with 100 per cent carbon monoxide steam/gas ratio of 3.0, at flow rates 10, 20 and 30 l./hr. and temperatures 365 and 340°C. The exit gas after condensing the steam was analysed by means of a precision Orsat apparatus. However, when the concentration of carbon dioxide in the gas was low, it was absorbed in a sodium hydroxide solution contained in three specially designed absorbers in series as described by Temkin.⁴ The whole set of measurements were repeated till constant values of conversion under a particular condition were obtained.

The rate constant k_1 was calculated from the following equation assuming a first order reaction⁵.

$$k_1 = -V(R + 1) \ln \left(1 - \frac{\eta}{\eta_{eq}}\right),$$

where V = space velocity in terms of c.c. of gas at NTP/hr./g. reduced catalyst.

R = Steam/gas ratio.

η = degree of conversion.

η_{eq} = degree of conversion at equilibrium, calculated from the equilibrium constant K of the reaction:



for $\text{H}_2\text{O}/\text{CO} = 3$.

K at different temperatures was calculated from the equation⁶.

$$\log_{10} K_p = \frac{2188}{T} + 0.0941 \log_{10} T - 0.632 \times 10^{-3} \times T + 1.086 \times 10^{-7} T^2 + 2.288,$$

where K_p is the equilibrium constant of the reverse reaction



T is the temperature in °K and $K = \frac{1}{K_p}$

The first order rate constant, thus calculated, was found to be a continuously decreasing function of the degree of conversion. Fig. 2 gives the results for two catalysts at 365°C. The values of rate constants were extrapolated to 0 at both the temperatures, viz. 365 and 340°C, to carry out the comparison of the activities of the catalysts under similar conditions. The activation energy E was calculated from the equation

$$E = \frac{2.303RTT'}{T - T'} \log \frac{k_1}{k_1'}$$

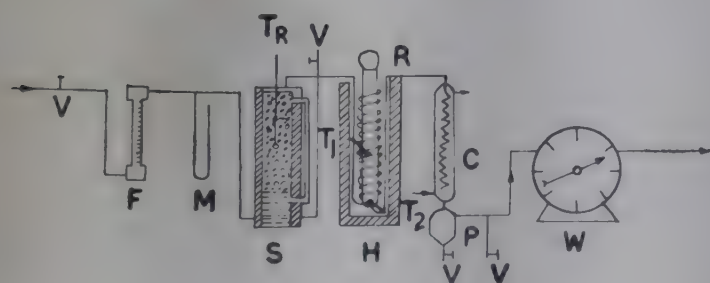
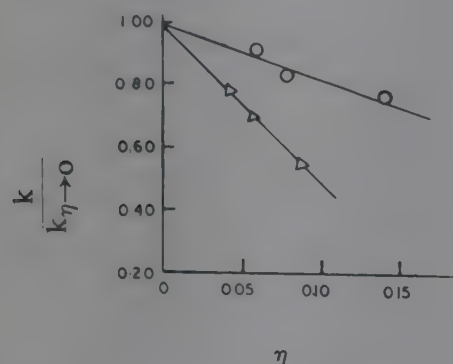


Fig. 1—Apparatus for Determining Catalytic Activity
V—Valve, F—Rotameter, M—Manometer, S—Saturator,
TR—Thermometer, R—Reactor, H—Reactor Furnace,
T₁, T₂—Thermocouples, C—Condenser, P—Condensate Trap,
W—Wet Gasmeter

TABLE 1—REDUCED SAMPLES

Sample	Vol. of He Displaced, V_{He} cc./g.	Vol. of Hg. Displaced, V_{Hg} cc./g.	Pore Volume V_p , cc./g.	Surface Area (BET), $M^2/g.$	$\bar{r}_p$ Å	$\bar{r}_g$ Å	Cr_2O_3 (unreduced sample) %	Loss on Ignition at 950°C (unreduced sample), %
A	0.2080	0.5992	0.3912	33.4	234.2	538.2	7.74	15.95
B	0.2018	0.4668	0.2650	30.7	172.6	456.2	6.56	11.21
C	0.1976	0.4268	0.2292	19.5	235.0	656.7	10.20	2.88
D	0.1802	0.4218	0.2316	12.2	379.7	1012.6	10.10	1.20
E	0.1841	1.1430	0.9589	7.5	2557.1	4572.5	Nil	25.01
F	0.2089	0.5292	0.3203	30.9	207.3	513.7	8.63	8.06
G	0.1737	0.5573	0.3836	27.9	274.9	599.2	10.30	7.18
H	0.1945	0.4160	0.2215	8.2	540.2	1521.9	10.10	0.95

where k_1 and k_1' , are rate constants at temperatures T and T' respectively.

Fig. 2—Variation of $k/k_{\eta \rightarrow 0}$ with Degree of Conversion

Surface area measurements were carried out by BET method in an all-glass high vacuum apparatus using nitrogen as adsorbate. Pore volumes were calculated from the differences in densities in helium and mercury as suggested by Anderson *et al.*⁸ The apparatus used for the determination of densities in helium was the same as described by Kokes⁹. Densities in mercury were determined separately. The average grain and pore radius $\bar{r}_g$ and $\bar{r}_p$ respectively were calculated from the following equations:

$$\bar{r}_g = \frac{3}{S \times D}, \quad \bar{r}_p = \frac{2V_p}{S},$$

where V_p = Pore volume.

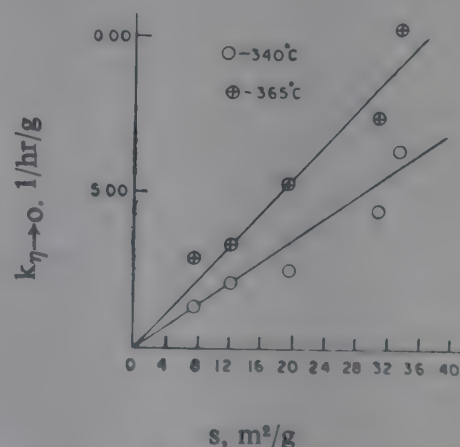
S = Surface area

D = Density in mercury i.e. particle density.

Results and Discussion

From the data (Table 2), it can be seen that the activity expressed as $k_{\eta \rightarrow 0}$ of five samples tested depends upon surface area of the reduced samples. The relationship

between the activity and surface area in this case is a linear one (Fig. 3). A similar observation has also been made by Mars¹⁰. However, samples F, Q and H show considerable deviation (Table 3). Uchida¹¹ also could not find any relationship between the catalytic activity and total surface area of the reduced catalysts. According to him, the following factors may influence the catalytic activity and so a simple relationship between activity and surface area is not observed: (a) The mobility of Fe and O atoms determines the ease with which the needle-shaped crystals of ferric oxide can be transformed into bigger grains of ferric oxide during reduction¹¹. This can partially explain the low activity of sample H which has been cured at high temperature, thereby fixing iron and oxygen atoms in their respective positions. (b) According to Yoshimura¹², the growth of ferric oxide particles during $Fe_2O_3 \rightarrow Fe_3O_4$ transformation is arrested in presence of Cr_2O_3 , thus increasing the surface area of active Fe_3O_4 -phase whose activity per unit area is a constant. This means that the activity of Fe_2O_3 - Cr_2O_3 catalysts will increase with increasing concentration of

Fig. 3—Activity of Iron Oxide/Chromium Oxide Catalysts ($k_{\eta \rightarrow 0}$) as a Function of Surface Area

TABLE—2

Sample	$k_{\eta \rightarrow o}$ l/hr		E, K Cal/mole	Specific Activity, cc/hr m ²	
	340°C	365°C		340°C	365°C
A	6.32	10.16	14.70	189.2	292.4
B	4.40	7.36	15.93	143.2	240.0
C	2.48	5.24	23.17	129.2	268.8
D	2.08	3.28	26.40	169.6	273.2
E	1.28	2.84	24.69	170.8	378.4

TABLE—3

Sample	$k_{\eta \rightarrow o}$ l/hr		E, K Cal/mole	Specific Activity, cc/hr/m ²	
	340°C	365°C		340°C	365°C
F	3.24	6.12	29.70	104.8	200.4
G	2.32	4.88	23.04	92.0	175.2
H	0.72	1.36	19.70	87.6	165.6

Cr₂O₃. However, the degree of increase of Fe₃O₄ surface and therefore the catalytic activity depend not only upon the concentration of chromic oxide but also upon the mode of its incorporation in the catalyst. Addition of potassium dichromate for incorporating Cr₂O₃ has been found to be more effective than the addition of CrO₃ in arresting growth of Fe₃O₄ crystallites due to better distribution of Cr₂O₃¹⁴. However, above a certain concentration of Cr₂O₃ (about 3 per cent) further increase in catalytic activity is not observed. In some cases the catalytic activity tends to fall at higher concentration of Cr₂O₃ due to partial coverage of active Fe₃O₄ surface by Cr₂O₃ layer. (c) Crystallographic modification of Fe₂O₃ phase affects the activation energy E. Parravano¹⁴ has shown that with γ -Fe₂O₃ E = 16.5 — 12.0 K cal/mole and with α -Fe₂O₃ E = 26.0 K cal/mole. Uchida¹⁰ has also found greater catalytic activity with Fe₃O₄ produced from γ -Fe₂O₃ than with that produced from α -Fe₂O₃.

In view of above, the surface of commercial CO-conversion catalyst cannot be treated as homogeneous. The number of active sites per unit area is governed by the method of preparation also. Thus, it can be concluded that although in some cases the catalytic activity of a commercial CO-conversion catalyst depends upon the surface area, departures are also not uncommon. Thus, a general relationship cannot be established in this case and the surface area data can be utilized for qualitative assessment of catalytic activity only if the methods of preparation are not widely different.

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A study on the nature of complex formation of trivalent cobaltic ion starting with two forms of biuret has shown that irrespective of forms taken, the biuret molecule is in *cis* configuration. Further, the complex was found to be diamagnetic in nature and the electronic spectral assignments showed that biuret occupies a position above cyanide ion in nephelauxetic series.

Absorption Studies on Cobaltic Biuret Complex

By R. M. SANYAL, A. K. CHAKRABORTY, S. C. SINHA
AND S. K. GHOSH,

*Planning & Development Division,
The Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

This laboratory has been investigating on the complex formation of biuret with metal ions with a view to develop a quick and accurate method of estimation of biuret in commercial urea^{1,2}. It is known that biuret molecule exists in two configurations, viz. *trans* or α and *cis* or β and they may form complexes with the trivalent metal ions. Cavalca³ et al have shown that in bis-biuret cadmium complex, the biuret is in *trans* configuration. Freeman, Smith and Taylor⁴ have suggested the *cis* configuration in the case of copper (II) chloride. Aida⁶ reported that biuret is in the *trans* form in the case of cadmium and mercury complexes, while in manganese and nickel complexes it is in the *cis* form. It has been stated earlier⁶ in case of a trivalent metal ions like Co^{3+} that the biuret is in the *cis* form. It can be seen from the works stated above that biuret molecule is in different configuration in the case of different metal ions, which is due to the internal rotation about the two C-N links of the biuret and influence of co-ordination.

Although two forms of biuret molecules are known, no attempt has been made to study the nature of biuret configuration used as a starting material and final configuration of biuret molecules after co-ordination. The present investigation is undertaken with a view to study this aspect of complex formation by using both the forms of biuret as starting material in the case of trivalent Co^{3+} ion.

Further, in our earlier works we have determined crystallographic data as well as molecular structure of

cobaltic biuret complex, but no electronic spectral assignment was made, which has been attempted here to have a complete picture on the structure of complex formed between biuret molecule and metal ions.

Experimental

The two forms of biuret which differ very much according to their recrystallizing condition were prepared. α and β forms were obtained by recrystallizing from water and ethanol solution respectively. The complexes were prepared following our previous method⁶ by taking α and β biurets as starting materials. Both forms of biuret and their respective complexes were studied in the solid phase by potassium bromide disc technique using the Perkin-Elmer infrared dual grating spectrophotometer model 421. The observations were taken in the region of 2.5 to 18 μ using strip chart recorder, scanning speed was about 17 min. or full range.

The visible spectrum was recorded in Beckman DU2 spectrophotometer using hydrogen and tungsten lamp the source at medium sensitivity.

The magnetic measurements were made on a Faraday type magnetic balance with an electrodynamic balancing system. The electro-magnet used in the set-up had specially shaped pole pieces designed after Sucksmith⁷.

Results and Discussion

(1) *Infrared Studies*: The infrared spectra of α and β biuret and their complexes with cobaltic ion are re-

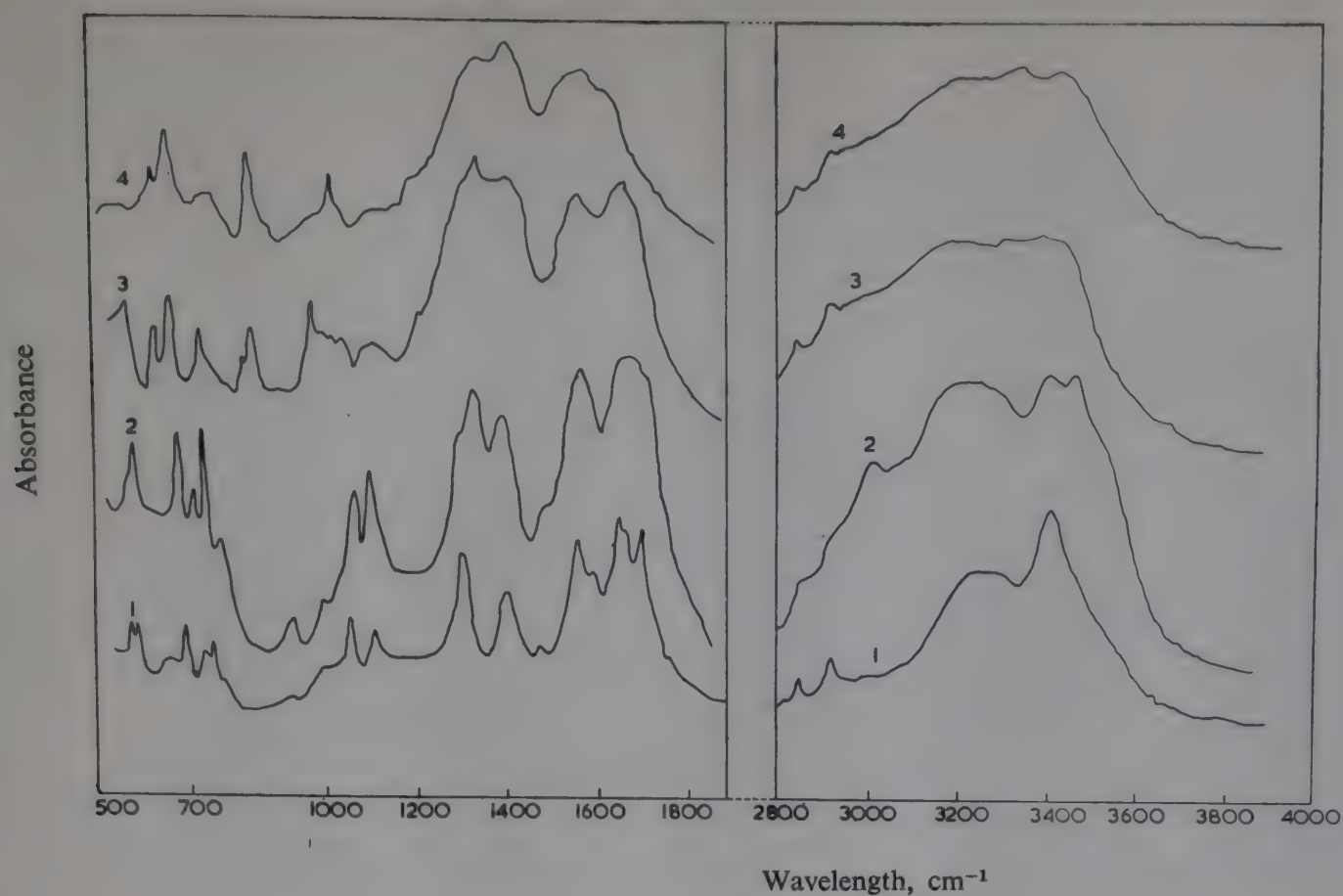
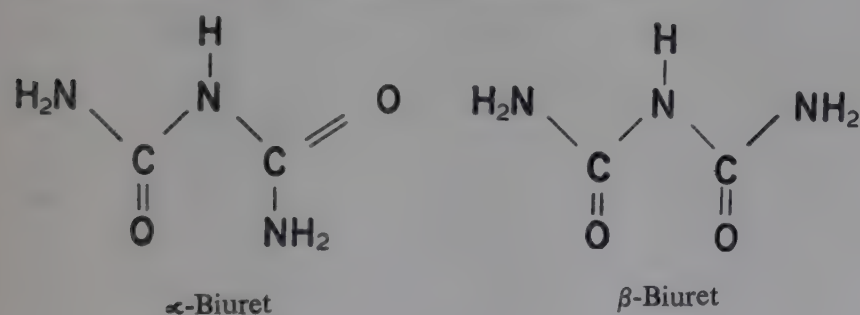


Fig. 1—Infrared Spectra of α and β Biurets and Their Complexes

produced in Fig. 1, Biuret molecule which exists in two configurations viz. α and β represented by:



and the two forms can be distinguished by their characteristic infrared spectra. The infrared spectra of the complexes prepared from these two forms of biuret did not show any change in the frequencies, which indicates that irrespective of the forms of biuret used as ligand always result in a *cis*-complex. Also, the behaviour of the spectra in 3 and 6 μ regions indicates that the biuret molecules are co-ordinated through the nitrogen atom of the end NH group of the biuret molecule, the detail molecular structure of which has already been published⁶.

(2) *Magnetic & Visible Spectral Studies*: Visible spectrum of cobaltic biuret complex made out of two forms of biuret were also studied. Both the spectra are similar in nature with no change in peak positions (Fig. 2).

It has been observed experimentally that in the complex, the metal-to-ligand ratio is 1:3, and the complex is diamagnetic. Cobalt atom has electron configuration $3d^7 4s^2$ and as such Co^{3+} would be $3d^6$ and has moment corresponding to four unpaired spins for weak ligand

fields. The majority of the octahedral cobaltic complexes are known to be diamagnetic in character because of spin pairing under the influence of ligand field. The complexes, under study in this context, appear to be spin-paired octahedral with $3d^2 4s 4p^3$ orbital hybridization.

The octahedral nature of the complexes are further confirmed by electronic absorption spectra. The bands are observed at 27,777, 20,408, 16,000 and 14,993 cm^{-1} . The first two bands are strong whereas the latter two are weak. The two strong bands can be readily assigned to the two spin allowed transitions $1A_{1g} \rightarrow 1T_{2g}$ and $1A_{1g} \rightarrow 1T_{1g}$. The weak bands are the spin forbidden transitions $1A_{1g} \rightarrow 3T_{1g}$ and $1A_{1g} \rightarrow 3T_{2g}$. These assignments have been made on the basis of $\text{Co}(\text{en})_3^{3+}$, because its spectra⁸ has similarity with the structure under study, except for a little difference in the band positions. However, the observed band at 14,493 cm^{-1} of the complex is missing in $\text{Co}(\text{en})_3^{3+}$. By using the descent in symmetry

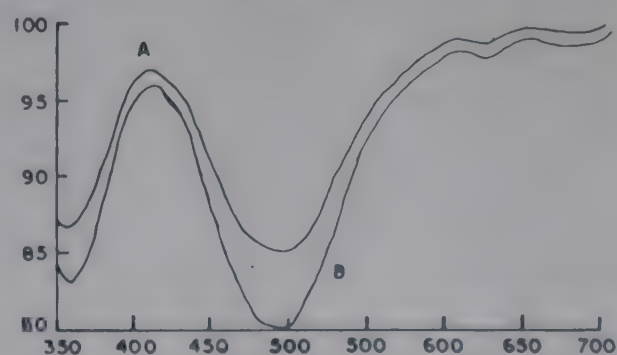


Fig. 2—Visible Spectra of Two Forms of Cobaltic Biuret Complex
A—*Trans* form, B—*Cis* form

method⁹, it is found that in the strong field approximation, we have,

$$\Delta E(1_{T_{2g}} - 1_{A_{1g}}) = 16F_2 - 115F_4 + 10 Dq \quad (1)$$

$$\Delta E(1_{T_{1g}} - 1_{A_{1g}}) = - 35F_4 + 10 Dq \quad (2)$$

$$\Delta E(3_{T_{1g}} - 1_{A_{1g}}) = - 105F_4 + 10 Dq \quad (3)$$

$$\Delta E(3_{T_{2g}} - 1_{A_{1g}}) = 8F_2 - 245F_4 + 10 Dq \quad (4)$$

From the first three equations, we obtain

$$10 Dq = 22613 \text{ cm}^{-1}$$

$$F_4 = 63 \text{ cm}^{-1}$$

$$\text{and } F_2 = 775 \text{ cm}^{-1}$$

The value of ligand field stabilization energy (LFSE)¹⁰ calculated from above values comes out to be 98 KCal/mol. Knowing F_2 and F_4 , the values of Racah parameters¹² B and C are calculated 460 and 2205 cm^{-1} respectively.

The values of B in the complexes are observed to be reduced from the corresponding gaseous ion value¹³ 1100 cm^{-1} as a consequence of co-ordination. The value of, β which is the ratio between the values of B in the complex and in the corresponding gaseous ion, reduces to 0.42. With this value of, β biuret occupies a position above cyanide ion in the nephelauxetic series¹¹ as mentioned: $F^- < H_2O < \text{Urea} < NH_3 < en \sim OX^{2-} < NCS^- < Cl^- \sim CN^- < \text{Biuret} < Br^- < I^- < dtp^-$

In the light of above magnetic and optical observations, it may be concluded that irrespective of nature of

biuret molecule chosen, the final product will always be octahedral in nature with all parameters remaining same.

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Polarographic studies on biuret in different supporting electrolytes of varying pH (1.0-13.0), show that biuret has dissociation constants $pK_1 = 9.2$, $pK_2 = 12.15$ involving ionization of two hydrogen atoms from the terminal $-NH_2$ groups. On adding increasing concentrations of biuret to cadmium (II) solution in ammonia buffer, the $E_{1/2}$ values shift towards more positive potentials and the i_d goes on decreasing. The shift towards more positive potentials is due to dimerization of the product of electrode reaction, the dimer being inactive at the d.m.e. The inactivation rate constant has been calculated (9.1×10^{-3} moles/l.).

Polarographic Studies on the Mode of Ionization and Chelation of Biuret

By M. B. MISHRA AND B. K. BANERJEE,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

In the recent past, attempts have been made to study biuret reaction with copper and other metal ions¹⁻³ using spectrophotometric and colorimetric techniques. However, no attempt has so far been made to study the anodic oxidation behaviour of biuret on the dropping mercury electrode. Also, the dissociation of biuret leading to its complexation with various metal ions has aroused controversy. Three probable modes of its chelation have so far been reported, viz. through $C=O$ group (of biuret) only, through ionization of one H atom from terminal $-NH_2$ groups, and through both $C=O$ and $-NH_2$. However, there does not at present exist a satisfactory solution of all these problems. The present studies were, therefore, undertaken with a view to evaluate the ionizations and electrode behaviour of biuret, and the rate constant, electrode reaction of its cadmium (II) complex, and the same are incorporated in this communication.

Experimental

Stock solutions of biuret (in minimum potassium hydroxide), cadmium chloride, hydrochloric acid, potassium chloride, acetic acid, ammonium acetate, phosphoric acid, trisodium orthophosphate, ammonia (liquor), ammonium chloride, sodium carbonate, sodium bicarbonate and sodium phosphate were prepared from

A. R. grade chemicals and were used from time to time. However, the ionic strength of the cell mixture was kept constant (0.2 M) except at pH 12.25 and 13.00, where it could not be maintained.

All the polarograms were recorded on an automatic recording Cambridge Univector polarograph unit using D. C. mode and dropping mercury electrode (d.m.e.). Mercury pool anode was used during all the measurements. Oxygen-free, dry nitrogen was bubbled through the solution for 5-10 min. to drive off dissolved oxygen and a dipping annulus type cell was used to maintain nitrogenous atmosphere over the solution during recording time. The drop time was 4.7 secs. The height of the mercury reservoir head was kept constant except during diffusion control studies. Double distilled water was used for preparing all solutions. Damping was 3; compensation and counter-currents were nil. All the measurements were carried out at $30 \pm 0.1^\circ C$.

Results and Discussion

Biuret gave a single well-defined reversible anodic wave in different supporting electrolytes of pH 1.0-13.0 (Fig. 1, Table 1). The characteristics of these waves have been summarized (Table 1).

Typical polarographic waves of biuret in carbonate buffer (pH 9.9), phosphate buffer (pH 7.0), acetate

buffer (pH 4.67) and hydrochloric acid (pH 1.0) are given in Fig. 1*. The system is reversible.

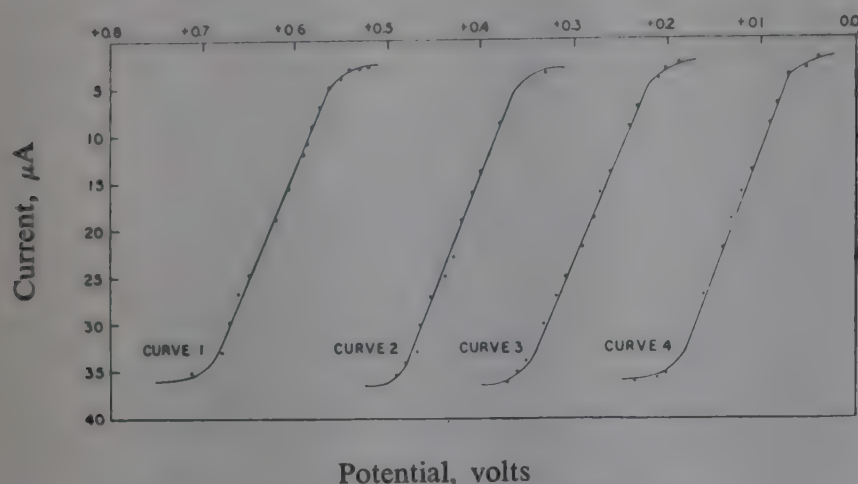


Fig. 1—Polarograms of 1.66×10^{-3} M Biuret

- Curve 1—Hydrochloric Acid (pH 1.0)
 Curve 2—Acetic Acid+Ammonium Acetate (pH 4.6)
 Curve 3—Phosphoric Acid+Trisodium Phosphate (pH 7.0)
 Curve 4—Sodium Carbonate+Sodium Bicarbonate (pH 9.9)

TABLE 1—POLAROGRAPHIC ANODIC WAVES OF BIURET
 IN VARIOUS SUPPORTING ELECTROLYTES
 [Ionic strength = 0.2M]

Sl. No.	Supporting Electrolyte	pH	$E_{\frac{1}{2}}$, Volts	$i_d/h^{\frac{1}{2}}$	pK
1.	Hydrochloric acid	1.0	+0.62		
2.	Hydrochloric acid + potassium chloride	2.0	+0.56		
3.	Acetic acid + ammonium acetate	4.6	+0.42		
4.	Phosphoric acid + Trisodium phosphate	7.0	+0.28	Constant $p_{K_1}=9.2$	
5.	Ammonia + Ammonium chloride	9.2	+0.16		
6.	Sodium carbonate + Sodium bicarbonate	9.9	+0.13		
7.	Sodium carbonate	11.2	+0.105		
8.	Trisodium phosphate	12.0	+0.080		
9.	Sodium hydroxide	12.25	+0.080**		$p_{K_2}=12.15$
10.	—do—	13.00	+0.080**		

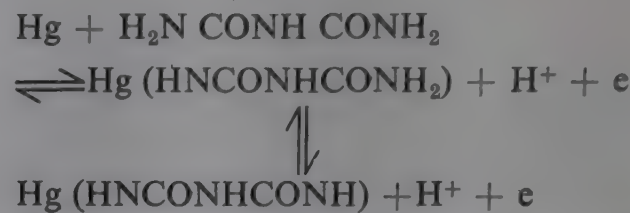
$E_{\frac{1}{2}}$ vs pH Graph: The half-wave potentials of the anodic waves of 0.166 mM biuret were plotted against pH (Fig. 2). The point of intersection of the straight lines gave the value of dissociation constants (pK_1 and pK_2) of $-NH_2$ group in biuret, viz., 9.2 and 12.15 respectively. The slope of the line (basic range) was 0.03 V

* Initial curves from the recorder were analysed and plotted on a broader scale.

** The ionic strength could not be maintained.

per unit increase of pH, which indicated clearly that only two hydrogen ions of biuret are taking part in the electrode reaction, whereas in acidic medium the slope being 0.06 V, indicates dissociation of only one hydrogen.

Mercury (II) is known to form complex with biuret. Considering the above facts, the reaction at the electrode can be given by the following equation:



(where charge contribution of biuret is neglected.)

The two electron oxidation and two hydrogen ion exchange support this mechanism. However, the polarograms in base media were followed by uniform current and preceded by a couple of maxima, whereas in acid media the maxima were observed after the oxidation (diffusion controlled current) process and uniform current preceded the current due to electrode reaction proper. The constancy of $i_d/\sqrt{h}$ values indicated that the waves are diffusion-controlled. Malik et al¹ have observed earlier that on plotting $E_{\frac{1}{2}}$ vs pH, the point after pH 12.04 does not lie on the straight line. Also, it has been observed that the mode of chelation of biuret is different above pH 12.04.

Cd—Biuret Complex: Cadmium (II) in phosphate buffer, pH (7.0), gave a single well-defined reversible wave, the $E_{\frac{1}{2}}$ of which is observed to shift towards more positive potentials with increasing concentrations of biuret being added to this solution (Table 2). A similar shift towards more positive potentials is observed in ammonia buffer, as reported earlier by Mishra and Banerjee³.

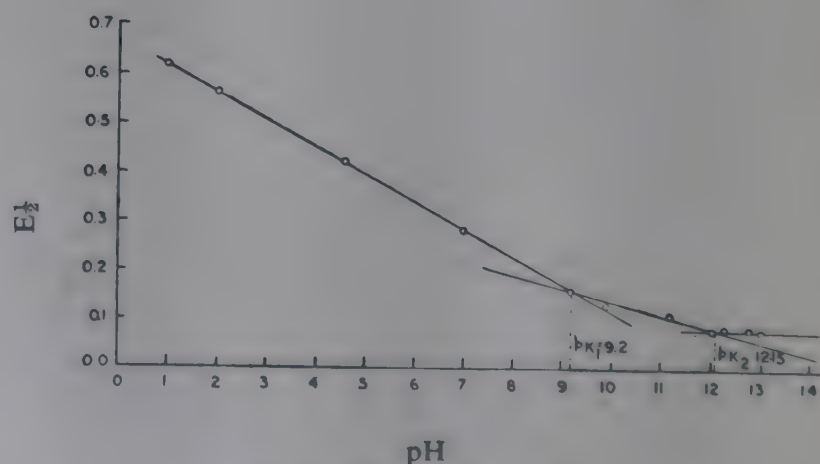


Fig. 2—Plot of $E_{\frac{1}{2}}$ Vs pH

phate or $\text{NH}_4\text{-K-polyphosphate}$ is formed. For example, 200 g. of crude, granular, K_2O . The mixture was boiled with stirring and replacement of evaporated H_2O for 30-45 minutes and filtered. The filtrate was allowed to cool to about 40°C . and 250 ml. of acetone was added with vigorous stirring. On standing overnight the mixture separated into two phases. The lower phase was sometimes present as a solid and sometimes as a viscous mass. In the latter case a solid was obtained by breaking up the mass and stirring. The solid was filtered off and dried in a vacuum oven at $40\text{-}50^\circ\text{C}$. The product was comprised of 140 g. of white amorphous solid containing P_2O_5 53.32, K_2O 20.62, and Na_2O 7.6 per cent. The average chain length was in the range 100-200 P atoms. One g of the product sequestered 130 ml. of standard Ca solution, equivalent to 0.052 g Ca.

[*ibid*, 124]

Nitric Acid Plant: D. R. Morrow (to Carrier Corp.), U.S. 3,441,380, Apr. 29, 1969, Appl. Oct. 22, 1965; 4 pp.

In the manufacture of HNO_3 by catalytic oxidation of NH_3 a refrigeration unit is used which utilizes energy evolved by the reactions to cool the reaction products and to decrease the temperature of the absorption tower. A compressor driven by the steam and hot gas turbines is used to compress the refrigerant. The compressed refrigerant is then cooled by the tail gas from the absorption tower, preheating the tail gas before it is heated in the combustion chamber. The refrigerant is used to cool the oxide after it emerges from the economizer. The refrigerant is also used to cool the absorption tower, providing more efficient absorption and higher strength acid and allowing the use of a smaller tower. Finally, refrigerant is used to cool the compressed air between compression stages to decrease the power required to drive the compressors.

[*ibid*, 2 (7) (1969), 147]

Linde AG Uses Nitrogen for Thermal Exchange in Space Simulator

In the space simulation chamber, which is to be erected for the French space-flight organization, Centre National d'Etudes Spatiales (CNES), by Linde AG. Werksgruppe Munchen of West Germany, the wide range of temperature extremes required, between -310° and 752°F , will be generated and maintained by the use of gaseous and liquid nitrogen as the thermal exchange media. It has also been stated

that nitrogen will be employed in the "cryopumps", which are used to generate vacuum conditions efficiently in the chamber.

The simulator, which will be Europe's largest space simulation chamber, is to be erected at the CNES research centre at Toulouse Lespinet and is estimated to cost DM 18.5 million. Design engineering has already begun and the start-up date is set for summer 1970. Another major contractor for the venture, in conjunction with Linde AG, is the French company, Societe Generale du Vide (SOGEV).

[*Nitrogen*, No. 59 (1969), 48]

Sulphuric Acid Process

Newton Chambers Engng Ltd. of U.K. have signed a licensing agreement with V/O Licensintorg, Moscow, which covers the design construction and marketing of sulphuric acid plants using carbon monoxide process system. The process is said to be of particular use where the raw material is pyrites or anhydrite but can also be applied to other feedstock. It is most advantageous where the feedstock produces a dirty gas. It eliminates the need of many gas-cleaning stages associated with ore-roasting acid plants and to simplify the acid cooling and absorption sections of the plants. Capital cost savings of between 15 and 20 per cent can be achieved with this process over the conventional methods. It has been operated successfully on a commercial scale for more than 7 years and a number of large plants are currently under construction in the USSR.

[*Indian Chem. J.*, 3 (12) (1969), 40]

Labelled Fertilizers

To meet the varied needs of the agricultural research institutions in this country in regard to radioisotopes and labelled compounds for improving agricultural methods and controlling pests, the Isotope Division of the Bhabha Atomic Research Centre, Bombay, has added to its range of preparations. Among them are fertilizers, such as superphosphate, triple superphosphate, nitrophosphate and mixed fertilizers labelled with radioisotopes. Since research investigations using these as tracers have provided valuable data about optimum fertilizer intake in different soils at different stages of plant growth, more and more agricultural research institutions are finding them useful.

[*Nuclear India*, 8 (2&3) (1969), 1]

Agricultural Association

Delegates from 40 agricultural institutions in India met in New Delhi under the auspices of the Post graduate School Students' Union of the Indian Agricultural Research Institute for setting up a professional body, named as Agricultural Association of India, under the patronage of Dr. B. P. Pal, Director-General ICAR, Dr. M. S. Swaminathan Director IARI, Dr. O. P. Gautam, Dy. Director ICAR, and all Vice-Chancellors of the Agricultural universities. The conference was inaugurated by the Union Minister of Parliamentary Affairs, Mr. K. Raghuramaiah, and was addressed by Mr. A. P. Jain, Chairman of the Irrigation Commission, and Mr. Asoka Mehta M.P. and former Union Minister for Petroleum and Chemicals.

One of the resolutions adopted by the conference urged that the Agricultural Association should be the body for undertaking registration of agricultural practitioners on the model of registered medical practitioners. The nationalized bank should give credit to the registered practitioners for equipping themselves with basic requisites like microscope, soil testing kit, etc. By another resolution the conference suggested that every agricultural college should adopt one village, preferably under dry farming, every year.

FCI at International Fair

Fertilizer Corpr. of India participated in the Second Asian International Trade Fair held at Teheran (Iran) during October 1969 by putting up two separate displays, viz. one in the Indian Pavilion and other in the Petrochemical Industries Hall organized in the International sector. While in the Indian Pavilion, the display was of a general nature with accent on export items, like catalysts, methanol and other chemical products from the Planning & Development Division and Trombay unit, in the International sector the display was of a more technical nature. The displays in the stall earned good comments from the Shah of Iran and other prominent visitors.

The wide range of FCI activities from production of fertilizers to the actual designing and erection of fertilizer plants was commended. The achievement in producing the whole range of catalysts for ammonia production came as a surprise to many visitors. Representatives from Jordan among others were impressed and made special enquiries regarding the particular spheres in which Jordan could benefit from Indian technology, parti-

cularly in the field of chemical industry. Many Iranian and other Middle East businessmen were interested in securing agencies for selling FCI fertilizers and chemicals in their markets.

[*FCI News*, 8 (1) (1970), 15]

FCI at EXPO '70

The display of Fertilizer Corporation of India in the International Fair being held at Osaka (Japan) has been arranged in the India Pavilion, which has a section devoted to petro-chemicals. It presents the activities of FCI from production of chemical fertilizers to catalysts and other chemicals, highlighting self-sufficiency in respect of fertilizer technology and our ability to build complete fertilizer plants on the basis of our own know-how and technology. The whole range chemical catalysts developed by the P and D Division on the basis of its own know-how finds pride of place in

the display, which has even impressed the Japanese fertilizer industry. A film on FCI dubbed in Japanese was also telecast.

[*FCI News*, 8 (2) (1970), 17]

Haldia Fertilizer Project

FCI's Rs. 74 crores project at Haldia (W. Bengal), for which preliminary agreements have been signed with M/s Montecatini-Edison of Italy on April 20, 1970, is likely to go on stream by the end of 1973. It will have facilities for the annual production of 165,000 te of urea, 379,000 te of (20-20) type NP fertilizers and 60,000 te of soda ash. It would draw its basic feedstock for production of ammonia from the adjoining refinery, now under construction, and proximity of Haldia docks would facilitate import of rock phosphate and salt from the south and west coast of India. The Planning & Development Division of FCI Ltd., which has made

much headway in the field of developing indigenous catalysts, would provide the necessary design and engineering facilities.

[*FCI News*, 8 (2) (1970), 9]

Methylamines Plant

India's first plant for the production of mono-, di- and trimethylamines will be set up by FCI Ltd. at Trombay. It will solve the problem of much-needed chemical intermediates required for the production of pesticides and rubber chemicals. It will go on stream in about 2 years' time and will lead to substantial savings in foreign exchange. The raw materials required are ammonia and methanol readily available. FCI Ltd., has signed an agreement with M/s Leonard Process Co. of USA and the Industrial Consulting Bureau Pvt. Ltd. for production of 4,000 metric tonnes of methylamines annually.

[*ibid*, 10]

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STATISTICS

TABLE 1—FAO REGIONAL INDEX NUMBERS OF FOOD AND TOTAL AGRICULTURAL PRODUCTION AND POPULATION

Region	1948-52	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968
1952-56=100																		
A. Food Production																		
Western Europe	84	93	101	101	102	103	106	109	113	119	118	126	128	130	130	134	144	147
Eastern Europe and USSR	83	91	94	96	104	114	118	129	131	133	137	140	134	146	149	167	168	176
North America	92	99	98	97	101	104	101	109	110	111	110	114	121	119	122	127	132	133
Oceania	92	98	99	99	104	110	97	118	115	121	124	135	138	144	136	158	145	173
Four above regions	87	95	98	98	103	107	107	115	117	120	121	125	127	131	133	142	146	151
Latin America	86	93	95	100	102	109	111	117	116	118	124	126	132	137	142	141	150	147
Near East	83	92	100	98	100	110	115	119	122	122	124	133	137	138	140	145	153	155
Far East (Excluding China (Mainland))	87	91	98	100	104	107	108	113	118	122	126	129	132	136	134	135	143	150
Africa	87	93	98	101	101	107	107	109	113	119	117	124	128	129	130	131	139	139
Four above regions	86	92	97	100	103	108	109	114	117	121	124	128	132	135	136	137	145	148
All above regions	87	94	98	99	103	107	108	115	117	120	122	126	129	132	134	140	146	150
B. Total Agricultural Production																		
Western Europe	84	93	101	101	102	103	106	109	112	119	118	126	128	129	130	133	143	145
Eastern Europe and USSR	82	90	94	96	105	115	118	128	130	132	135	138	133	145	148	165	167	174
North America	93	99	99	97	101	103	98	106	107	109	109	112	119	117	119	120	124	126
Oceania	90	96	97	98	104	105	101	118	119	122	125	133	137	141	135	151	144	164
Four above regions	87	95	98	98	103	107	106	113	116	119	119	124	126	130	131	138	142	147
Latin America	87	94	95	100	103	107	111	118	118	121	128	130	133	136	142	140	147	144
Near East	84	93	99	98	100	110	115	118	123	124	124	135	139	142	145	149	155	158
Far East (excluding China Mainland)	87	92	97	100	104	107	108	112	117	121	126	128	131	135	133	135	142	149
Africa	86	93	97	101	102	107	108	110	115	122	119	127	131	133	135	135	144	143
Four above regions	86	93	97	100	103	108	110	114	118	121	125	129	133	136	137	138	145	148
All above regions	87	94	98	99	103	107	107	114	116	120	121	126	129	132	133	138	143	147
C. Population																		
Western Europe	97	99	99	100	101	102	102	103	104	105	106	107	108	109	110	111	112	113
Eastern Europe and USSR	95	97	98	100	102	103	105	106	108	109	111	112	114	115	116	117	118	119
North America	93	96	98	100	102	104	106	108	109	111	113	115	117	118	120	122	123	124
Oceania	91	95	98	100	103	105	107	110	112	115	117	120	122	125	127	130	132	135
Four above regions	95	97	99	100	101	103	104	105	107	108	110	111	112	114	115	116	117	118
Latin America	90	95	97	100	103	106	108	112	115	118	121	125	128	132	136	140	144	148
Near East	90	95	98	100	102	105	108	111	113	116	119	122	125	129	132	135	139	143
Far East (excluding China Mainland)	93	96	98	100	102	104	106	109	111	113	116	119	122	125	128	131	134	137
Africa	91	96	98	100	102	105	107	110	113	116	118	121	124	127	131	134	137	141
Four above regions	92	96	98	100	102	104	107	109	112	115	117	120	123	127	130	133	136	140
All above regions	93	96	98	100	102	104	106	108	110	112	114	117	119	122	124	127	129	132

[Monthly Bull. of Agricultural Economics and Statistics, 18 (July/August) (1969), 14]

TABLE 2—FAO COUNTRY INDEX NUMBERS OF PER CAPUT FOOD PRODUCTION

Region and Country	Per Caput Food Production																
	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968
<i>Europe</i>																	
France	91	100	106	101	101	100	101	105	117	112	122	118	119	126	121	139	143
Germany Fed. Rep. of	97	101	102	100	100	100	107	100	114	100	112	116	112	103	110	119	123
Italy	92	104	96	104	103	101	114	114	106	117	117	109	117	118	121	126	123
Netherlands	100	99	100	105	96	101	105	103	115	110	119	110	109	104	106	115	120
Sweden	104	105	102	91	98	96	93	94	98	96	99	92	98	96	87	98	101
United Kingdom	95	98	100	99	107	106	105	111	117	118	126	127	132	134	136	139	134
Yugoslavia	72	120	89	118	100	141	117	160	138	125	129	139	142	132	163	156	151
<i>North America</i>																	
Canada	118	108	78	96	101	84	85	86	90	74	94	103	94	102	110	92	97
United States	101	99	100	100	101	97	103	102	101	100	99	104	102	102	104	109	108
<i>Oceania</i>																	
Australia	102	101	100	103	94	88	110	102	108	107	117	117	120	109	130	112	137
<i>Latin America</i>																	
Argentina	100	96	101	95	107	96	102	93	86	92	95	107	104	90	96	104	92
Brazil	94	98	102	102	104	108	109	108	110	112	112	112	115	123	117	120	118
Chile	96	99	99	103	103	97	107	98	98	101	98	103	101	94	94	94	94
Cuba	129	99	95	89	91	101	99	101	100	106	83	71	75	90	72	88	77
Mexico	88	94	102	105	109	120	125	119	119	123	122	123	126	126	125	127	125
<i>Far East</i>																	
Burma	103	99	97	97	104	89	103	108	106	107	114	112	118	110	95	104	109
India	93	103	100	102	102	100	102	105	106	107	105	104	103	96	93	98	101
Indonesia	94	100	107	100	100	99	102	101	101	96	102	93	100	96	97	92	95
Japan	100	87	94	111	107	109	114	113	113	113	122	119	121	121	125	137	141
Pakistan	101	102	102	96	100	99	96	100	101	99	96	101	98	97	92	97	100
Algeria	94	100	108	94	104	92	84	88	90	69	81	80	68	73	52	61	66
Israel	88	87	106	100	116	115	115	136	135	136	143	147	162	159	154	176	177
Morocco	96	105	108	93	98	82	99	88	90	70	92	94	94	96	76	83	117
United Arab Republic	89	95	104	104	107	107	102	104	108	99	113	112	110	109	111	106	110

[Ibid, 18]

TABLE 3—FAO COUNTRY INDEX NUMBERS OF PER CAPUT TOTAL AGRICULTURAL PRODUCTION

Region and Country	Per Caput Total Agricultural Production																
	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968
1952-56=100																	
<i>Europe</i>																	
France	91	100	106	101	101	100	101	105	117	112	122	118	119	126	121	138	142
Germany, Fed. Rep. of	97	101	102	100	100	100	107	100	113	100	111	115	112	103	110	118	122
Italy	93	104	96	104	103	100	113	113	105	114	115	108	115	117	119	124	121
Netherlands	101	99	99	105	96	100	103	102	114	109	118	110	109	103	105	113	118
Sweden	104	105	102	91	98	96	93	94	97	95	99	92	98	95	87	97	100
United Kingdom	95	98	100	99	107	106	105	111	117	118	126	126	132	133	135	138	133
Yugoslavia	72	119	90	119	99	140	116	157	135	122	127	138	141	130	160	154	146
<i>North America</i>																	
Canada	116	107	79	96	103	85	87	86	91	75	94	103	94	102	110	92	97
United States	102	100	99	100	99	94	99	99	99	98	98	102	99	99	98	101	102
<i>Oceania</i>																	
Australia	101	98	98	103	100	92	109	106	107	108	113	115	116	105	121	109	126
<i>Latin America</i>																	
Argentina	102	97	101	94	106	96	102	94	86	93	95	106	103	90	96	101	91
Brazil	98	98	99	104	100	106	110	115	115	118	119	111	107	120	111	111	108
Chile	97	99	99	102	102	97	106	99	98	100	97	102	100	94	94	94	94
Mexico	87	91	102	110	108	119	124	113	116	117	118	119	122	121	121	121	119
Burma	104	99	98	97	103	89	101	106	104	104	112	111	116	108	93	102	107
India	93	102	101	102	103	101	102	104	106	107	105	105	104	96	93	98	101
Indonesia	97	99	106	100	98	98	100	100	98	95	100	91	95	94	94	92	93
Japan	100	87	95	111	107	110	113	112	112	112	120	117	121	120	123	135	138
Pakistan	104	99	100	97	100	98	95	99	98	98	96	100	96	96	93	98	99
Algeria	94	102	108	94	102	91	82	87	89	67	79	78	66	72	54	61	66
Israel	88	88	106	100	116	117	117	140	141	145	151	152	169	169	166	190	192
Morocco	97	105	107	93	98	81	99	88	89	70	91	92	92	94	76	83	114
United Arab Republic	100	94	102	101	102	107	105	107	110	95	111	109	111	110	107	102	104

[ibid, 19]

TABLE 4—FAO COUNTRY INDEX NUMBERS OF TOTAL AGRICULTURAL PRODUCTION

Region and Country	Total Agricultural Production																
	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968
1952-56=100																	
Europe																	
Germany, Fed. Rep. of	95	100	102	101	102	103	112	106	121	109	123	128	126	118	127	137	144
Italy	92	103	96	105	104	102	115	116	109	119	121	114	123	126	130	135	133
Netherlands	98	97	99	106	98	104	109	108	123	119	131	123	124	119	123	134	142
Sweden	103	104	102	92	99	98	95	97	101	99	104	97	104	102	94	106	110
United Kingdom	95	98	100	99	108	108	107	113	120	122	132	133	140	143	145	149	145
Yugoslavia	70	117	90	121	102	145	121	166	144	132	138	152	157	147	183	178	171
North America (Canada)	110	104	79	99	108	92	97	99	107	90	114	127	118	130	144	122	131
United States	98	98	99	101	103	99	107	108	110	111	112	118	117	118	118	124	126
Oceania																	
Australia	97	96	98	105	105	98	119	118	122	126	134	139	144	132	154	142	167
Latin America																	
Argentina	98	95	101	96	110	102	111	104	97	106	111	124	123	110	118	126	116
Brazil	92	95	99	107	106	116	124	133	137	145	150	144	143	166	157	163	163
Chile	92	97	99	105	108	105	117	112	113	119	118	126	127	122	124	127	129
Cuba	121	97	95	92	95	108	107	112	114	122	100	96	94	113	94	115	103
Mexico	81	88	102	113	115	131	141	133	141	148	153	161	170	175	180	186	189
Far East																	
Burma	100	97	98	99	106	94	109	116	116	119	130	131	140	134	117	131	141
India	90	100	100	103	106	107	111	114	120	124	124	127	129	122	121	131	138
Indonesia	93	97	106	102	102	105	108	111	111	110	118	111	119	120	123	123	128
Japan	97	86	95	113	110	113	118	118	118	120	130	128	133	133	139	153	159
Pakistan	98	97	100	100	105	107	106	113	116	120	120	128	128	131	130	142	148
Philippines	92	96	100	103	109	113	113	115	123	126	135	140	139	146	156	160	164
Africa and Near East																	
Algeria	91	100	107	96	106	97	90	97	101	78	91	92	82	91	69	81	90
Israel	83	85	105	103	125	133	137	169	175	186	204	211	245	255	255	297	309
Morocco	92	102	107	96	103	88	110	101	105	86	114	119	121	127	106	119	169
United Arab Republic	95	92	102	103	107	115	116	120	127	112	135	136	141	144	144	140	147

[ibid, 17]

TABLE 5—FAO REGIONAL INDEX NUMBERS OF PER CAPUT FOOD AND TOTAL AGRICULTURAL PRODUCTION

Region	1948-52	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968
1952-56=100																		
A. Per Caput Food Production																		
Western Europe	86	94	102	101	101	102	104	106	108	114	112	118	118	119	118	120	129	130
Eastern Europe and USSR	88	94	96	96	103	111	113	122	122	122	123	124	118	127	128	143	142	148
North America	99	103	100	97	99	101	96	101	100	100	98	99	104	101	102	104	107	107
Oceania	102	103	102	99	102	96	91	107	102	106	105	113	113	116	107	122	110	129
Four above regions	92	97	99	98	101	104	103	109	109	111	110	113	113	115	115	122	125	128
Latin America	96	99	98	100	100	103	103	105	101	100	103	101	102	104	104	101	104	100
Near East	92	97	102	98	98	105	107	107	107	105	104	109	109	107	106	107	110	108
Far East (excluding China)	94	95	100	100	102	103	102	104	106	108	109	108	108	109	105	103	106	109
Mainland)	95	97	100	101	99	102	100	99	100	103	99	102	103	101	99	98	101	98
Africa																		
Four above regions	94	96	100	100	101	103	102	104	105	105	106	106	107	107	105	103	106	106
All above regions	93	97	100	99	101	103	102	106	106	107	106	108	108	109	108	111	113	114
B. Per Caput Total Agricultural Production																		
Western Europe	87	94	101	101	102	102	104	106	108	113	111	117	118	118	117	120	128	129
Eastern Europe and USSR	87	93	96	96	103	111	113	121	121	121	122	123	117	126	128	141	141	146
North America	100	103	101	97	99	100	93	98	98	98	96	98	102	99	99	99	100	101
Oceania	99	101	99	98	101	100	94	107	106	106	107	111	112	113	106	117	109	122
Four above regions	92	97	99	98	101	104	102	108	108	110	109	112	112	114	114	119	121	124
Latin America	97	100	98	100	101	102	103	106	103	102	105	104	104	103	105	100	102	97
Near East	93	98	101	98	98	105	107	107	108	107	104	111	110	110	110	110	112	111
Far East (excluding China)	94	96	99	100	102	103	102	103	105	107	108	108	108	108	104	103	106	108
Mainland)	94	97	100	101	99	103	101	101	102	106	100	105	105	104	103	101	104	101
Africa																		
Four above regions	94	97	99	100	101	103	103	104	105	106	106	108	107	107	106	104	104	106
All above regions	93	98	99	99	101	103	101	105	106	107	106	108	108	108	107	109	111	112

TABLE 6—FAO COUNTRY INDEX NUMBERS OF FOOD PRODUCTION

Region and Country	Food Production																
	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968
Europe																	
France	89	99	106	102	103	102	105	110	124	120	133	132	133	143	139	160	167
Germany Fed. Rep. of	95	100	102	101	102	103	112	106	122	109	123	129	127	118	127	138	145
Greece	82	106	101	103	109	125	119	127	118	136	130	140	156	161	172	174	165
Italy*	91	103	96	105	104	103	117	117	110	122	123	115	125	128	132	137	135
Netherlands	98	98	99	106	98	105	110	110	124	121	132	124	125	120	125	137	144
Sweden	103	104	102	92	99	98	95	97	101	100	104	97	104	102	94	106	111
United Kingdom	95	98	100	99	108	108	107	113	121	122	132	134	141	143	146	150	146
Yugoslavia	70	118	89	120	102	145	122	169	147	135	141	154	159	149	186	181	176
Canada	112	105	78	99	106	91	96	99	105	88	114	127	118	130	144	123	132
United States	98	97	99	102	104	103	111	111	112	113	114	120	120	121	125	133	134
Australia	98	99	100	105	98	94	120	114	123	125	139	142	149	137	167	146	182
Argentina	96	94	101	97	111	102	110	103	96	105	111	126	124	109	119	130	118
Brazil	88	95	102	105	111	118	122	125	131	137	142	145	154	170	166	176	178
Chile	91	97	99	105	108	105	118	111	114	119	118	128	128	122	124	128	130
Cuba	123	97	94	91	95	108	108	112	113	122	98	85	92	114	93	116	103
Mexico	83	91	102	109	116	132	142	140	145	154	158	165	175	182	186	195	199
Burma	100	97	97	99	107	93	111	118	118	121	132	133	142	136	120	134	143
India	90	101	100	104	106	106	111	116	120	124	124	126	128	122	121	130	139
Indonesia	90	97	107	102	104	106	111	113	115	112	122	114	124	123	127	124	131
Japan	98	86	95	112	110	113	119	118	120	121	132	130	134	135	141	156	163
Pakistan	96	99	102	98	105	107	106	115	119	120	120	130	130	132	130	141	149
Philippines	92	96	100	103	108	112	112	114	121	124	131	137	136	145	155	159	163
Algeria	90	98	108	96	109	98	91	98	102	81	94	95	83	92	67	80	90
Israel	83	85	105	102	124	131	135	165	167	175	192	204	235	239	237	276	284
Morocco	91	102	108	96	104	88	111	102	107	86	115	120	124	129	105	119	173
United Arab Republic	85	93	104	106	112	115	112	117	124	117	137	139	141	143	149	146	156

[ibid, 15]

TABLE 7—AREA AND PRODUCTION: NEW AND REVISED DATA RECEIVED DURING JUNE 1969

Commodity and Country	Year	Area	Production
		1 000 ha	1 000 m.t.
<i>Wheat</i>			
Bulgaria	1968	1 060	2 549
France	1969	4 060	14 715
Denmark	1969	49	—
Rumania	1968	—	4 848
Canada	1969	10 532	—
Mexico	1968	717	1 894
United Arab Republic	1968	—	1 518
Australia	1967	9 081	7 547
	1968	10 764	14 571
<i>Rice</i>			
Bulgaria	1968	14	39
Hungary	1968	21	41
Mexico	1967	170	430
	1968	167	455
Argentina	1969	—	335
Ecuador	1968	—	218
Cambodia	1969	—	2 253
Nepal	1968	—	2 322
Australia	1969	33	238
<i>Sugar Cane</i>			
United States	1968/69	—	11 562
Hawaii	1967/68	—	10 233

[ibid, 20]

TECHNOLOGY

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TECHNOLOGY, VOL. 7 (1970), NO. 3, JULY-SEPTEMBER

The following papers have been accepted for publication in the next issue of TECHNOLOGY, viz. 7 (1970), No. 3, July-September.

LABORATORY DETERMINATION OF SOIL DENSITY USING GAMMA RAY ATTENUATION

by B. S. Sastry, W. Sethuraman, K. Appalacharyulu, Om Sheel and K. C. Banerji

ROASTING OF FERRO AND FERROMANGANO-PHOSPHOROUS AND THEIR OXIDATION KINETICS

by H. Roy and S. K. Adhya

A NEW PROCESS FOR THE PREPARATION OF WATER-SOLUBLE PHOSPHATIC FERTILIZERS FROM IRON-RICH PHOSPHATIC ROCKS

by H. Roy, S. K. Adhya and S. K. Sharma

DEPENDENCE OF DESULPHURIZATION ACTIVITY OF ZINC OXIDE ON ITS STRUCTURAL PARAMETERS

by P. K. Gaur, A. R. Chatterjee, M. M. Chhabra and N. B. Bhattacharyya

A STUDY OF DESULPHURIZATION OXIDE

by M. Sundaram and N. B. Bhattacharyya

DEPENDENCE OF HYDROXYLATION ON THE SURFACE OF SILICA GEL CARRIERS

by R. N. Tiwari, S. R. Naidu, N. C. Ganguli and S. P. Sen

MECHANISM OF ALTERNATION OF PORE STRUCTURE OF SILICA GEL WITH DIFFERENT AMOUNTS OF A MODIFYING SALT

by Samir K. Ghosh and N. C. Saha

INFRARED ABSORPTION STUDIES ON $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{SO}_3$ SYSTEM: PART 2

by R. M. Bhatnagar, R. M. Verma, A. K. Chakravorty and A. K. Roy

INFLUENCE OF ADDITIVES ON THE HAZARDOUS BEHAVIOUR OF AMMONIUM NITRATE

by S. Varma and R. C. Saxena

STUDIES ON CATION-EXCHANGE RESIN FROM ACID SLUDGE: CATION-EXCHANGE EQUILIBRIUM

by B. K. Dutta and V. K. Seth

ECOLOGY OF SOIL FUNGI OF RICE FIELDS BY III-ANTAGONISTIC MICROORGANISMS OCCURRING ON PADDY ROOTS

by A. C. Das and N. K. Shaw

HYBRID ANNUNCIATOR CIRCUITS

by G. P. Gupta

scrubber containing a number of wooden grates. A solution of solution polysulphide and free sodium hydroxide at 36°C flows down the tower at a rate of 3 l./m³ of gas. Most of the solution obtained at the bottom of this tower is recirculated to the top, but about 15 per cent per cycle is fed through a preheater into a subsequent reactor.

In this reactor, pulverized sulphur and sodium hydroxide solution are added and the mixture produced is agitated at 80°C. Excess sulphur is removed in a settling tank at about 70°C and then the solution, containing 1 to 3 g. of sulphur and 15 to 20 g. of sodium hydroxide per litre, is cooled and returned as make-up to the scrubber. In this way the concentration of reactants in the circulating polysulphide solution is maintained.

Before the make-up liquid is returned to the scrubber, a small quantity is continuously drawn off as the raw thiocyanate product solution. This solution contains about 400 g./l. of sodium thiocyanide, 20 g./l. of sodium carbonate 30 g./l. of Na₂S₂O₃ and small amounts of other compounds.

Thiocyanate Purification: At Ostrava the sodium thiocyanate is removed from the raw solution by a chemical method. The raw thiocyanate solution is fed to the reactor, operating at 90 to 100°C, in which 90 to 93 per cent sulphuric acid is added in amounts corresponding to 0.455 g./g. of Na₂S₂O₃ and 0.925 g./h. of sodium carbonate. This mixture is boiled for 10 hours, after which time most of the impurities are converted to sulphates and free sulphur and the solid content of the mixture is roughly 750 g./l. The pH value of this slurry is then adjusted to between 7 and 8 by addition of sodium hydroxide, and the mixture is allowed to settle. Boiling with sulphuric acid liberates acids gases from the raw thiocyanate solution and these are washed with sodium hydroxide in a small scrubber before venting.

The precipitate which forms on settling is centrifuged and the filtrate obtained contains around 4 g./l. of sulphates, together with some metallic contaminants, particularly lead. This solution is then oxidized by bubbling air through it, and on adding barium hydroxide solution and sodium sulphide solution all sulphates and other impurities are removed. The resulting solution, which is dark in colour, is decolorized by adding 35 kg. of active carbon per tonne of thiocyanate. This solution is then agitated at 100°C and then finely filtered to give a pure solution of sodium thiocyanate.

Crystallization: The pure thiocyanate solution is evaporated up to a concentration of 860 g./l. and then cooled down to between 10 and 12°C so that crystallization occurs on standing. In this way about half of the thiocyanate present in the solution crystallizes out as white NaCNS. 2H₂O, and the remaining solution is centrifuged and recycled into the process.

The table below shows an analysis of the crystals produced by the process.

Water-insoluble substances, %	0.001 to 0.003
NaCNS, %	68.4 to 68.6
Iron, %	Max. 0.0002
Heavy Metals, %	Max. 0.002
Sulphur compounds, %	0.004 to 0.007
Chlorine, %	Max. 0.01
pH of 50% solution	6.5 to 7.4

[Nitrogen, No. 58, (1969), 35]

Rajasthan Pyrites

While delivering an address on 'Mineral Industry in India—a Plan for Seventies', under the auspices of the Indian Institute of Mineral Engineers at Kharagpur on Jan. 2, 1970, Sri Tej Bhan Malhotra, Managing Director, Uranium Corporation of India, Department of Atomic Energy, said that the pyrites deposits at Amjhore (Bihar) have very difficult mining conditions.

At Saladipura (Rajasthan) a massive deposit of pyrite and pyrrhotite has been discovered. The following are its characteristics: (1) It has large reserves and therefore has potential of meeting the entire requirements of the country for sulphuric acid for many years to come, if its geographical location makes it economically feasible. (2) The ore body appears to be relatively uniform and continuous and the wall rocks as well as ore body appear to be competent. Mining methods yielding large production and high productivity appear feasible and mining costs are expected to be comparatively low. (3) The massive mineralization of the ore is likely to lend itself to simple gravity methods of beneficiation. Possibly crushing to $\frac{3}{4}$ " with heavy media separation and jigging would yield a recovery of about 90 per cent of the sulphur in a grade of at least 42 per cent sulphur. This product should be ideal for railage and for use in pyrites roasters at points of consumption. (4) It should be possible to start production in about 4 years' time. (5) No exploratory mining as such appears necessary. Even drilling may be planned to prove only such re-

serves which will be needed in the foreseeable future.

Sri Malhotra estimated that the cost of producing pyrite concentrates at Saladipura containing 42 per cent sulphur should not exceed about Rs. 90/te delivered in wagons at the mine. He urged that this deposit should be opened without delay; at least two mines should be opened up in the area each with an initial capacity of 1000 te/day of run-of-mine ore to be increased to 3400 te/day in the second stage which should be completed by the end of this decade. Thus, by 1979, there will be a million tonnes of concentrates containing 42 per cent sulphur per annum saving foreign exchange worth Rs. 20 crores/year, providing direct employment to about 6000 persons and indirect employment to 20,000 persons.

Technical Personnel in a Developing Country

The U. N. Inter-regional Seminar on Employment, Development and Role of Scientists and Technical Personnel in the Public Services of Developing Countries, was held at Tashkent, USSR, during October 1-14, 1969, in which 27 countries participated and made very useful recommendations under the following six main heads:

1. *Role of Scientific and Technical Personnel within Public Sector:* The roles of scientific and technical personnel within the public sector should be defined. National personnel policies should provide establishments of senior posts open to scientists and other technical personnel which permit use of their specialized abilities and experience in administrative fields. High level scientists should be there to advise at top policy levels of government. Active encouragement should be given towards obtaining increased participation of scientists in conduct and use of research and development. Scientific and technical societies should be established or expanded for (i) mutual exchange and dissemination of knowledge and experience and (ii) participation in the creation and development of stronger national science policies, (iii) maintenance of contacts with foreign societies and (iv) participation in establishment of professional standards and traditions. Scientific and technical personnel should participate in the designing and development of the national economic plan.

2. *Status and Working Conditions of Scientific and Technical Personnel:* National science policies should be formulated as clearly and concretely as possible to

ensure their relationship to economic and social development goals. Scientists and technologists should be involved at every stage in formulation and in the implementation of such policies. Specific priorities and allocation of resources based on such policies should be reviewed periodically in terms of accomplishments and changing conditions. The productivity of individual workers and research organizations should be assessed in relation to their contribution to the fulfilment of national priorities and objectives. The establishment of favourable working conditions will enhance the creativity and productivity of all scientists at every level in the public services.

3. Administration of Public Personnel Systems to Ensure Maximum Effectiveness in Recruitment, Orientation, Placement, Promotion, Development Remuneration and Retention of Scientific and Technical Personnel: To ensure increased responsiveness to the career requirements of scientific personnel, their participation in personnel policy development and implementation is required. Two mechanisms have been proposed, viz. appointment of a scientist to the top management of the central personnel agency or the use of an advisory committee composed of scientific and technical reporting personnel to the highest level. A wide range of recruitment and appointment methods should be used to satisfy different requirements. Entry of qualified personnel from outside to the higher levels should be facilitated. Career and promotion opportunities should be based on professional evaluation of achievement independent of place in the administrative principle. Pay scales should be based essentially on the principle of equal pay for equal work, but they should incorporate an appropriate degree of flexibility. Consideration should be given to wider use of material and intangible incentives, such as honours, titles, etc. Some type of bonus system might be used to recognize outstanding achievement.

4. Policies and Programmes to Increase and Improve Motivation, Creativity, Leadership, etc.: To ensure effective performance and retention of scientific personnel, considerable attraction must be given to the total environment through such measures as (i) providing opportunities for association with colleagues throughout the world, (ii) keeping abreast of new development, and (iii) providing effective leadership and suitable working conditions. Adequate clerical and technical support service should

be given, which may include a sufficient number of laboratory technicians, clerks, skilled workers, financial supply and other services. Scientific resources should be directed towards specific national goals rather than science for the sake of national prestige. Maximum effort should be devoted towards fuller utilization of scientific and technical knowledge and more attention should be given by both scientific and political leaders to the growing volume of studies on the behaviour of scientists and engineers in research and development laboratories. To reduce the problem of migration of talent without inhibiting desirable mobility, the following steps should be taken: (i) offering challenging assignments, (ii) making better use of existing national specialist resources, (iii) soliciting support of international organizations and recipient countries to persuade migrant specialist to return to their home countries, (iv) planning objectives of overseas training programmes in terms of the country's needs and providing suitable posts upon return of students and (v) developing special programmes designed to retain or to recall scientists who have migrated. Developing countries should co-operate in the establishment of regional research organizations to pool their resources.

5. Improvement of Management National Civil Service Whose Staffing Includes Scientific Personnel: Opportunities for advancement to the top levels of the civil service should be for outstanding achievement independent of particular job level, age and seniority factors and primarily based on achievement in work performance should be formulated.

6. Career Planning and Career Development of Scientific Personnel: Representatives of the Government should work out career development policies and conditions regarding this type of personnel. Central Personnel Agency for the Government should be given the responsibility for designing, maintaining and evaluating the overall career development programme. Scientific personnel should be allowed to attend conferences, seminars, publishing of technical papers and preparation of professional texts. The development of well-organized information centres maintaining current information on science and technology results is essential for professional development.

Institutions of higher learning should be encouraged to provide facilities for the management development of public ser-

vants. To this end, the Government should offer such resources as funds for additional tutors, accommodation and equipment. Such management development programmes on a continuing basis should embrace preentry as well as in service training for serving offices to increase their managerial capabilities.

[*Tech. Manpower (CSIR)*, 9 (10) (1969), 1]

Indian Science

Inaugurating the 57th session of the Indian Science Congress at Kharagpur (W. Bengal) on January 3, 1970, Smt. Indira Gandhi, Prime Minister, suggested decentralization of scientific organizations in the country for better utilization of the talents of the young and aspiring scientists. Since the future of the Indian scientist is tied up with the future of the country, he should therefore be committed not only to the cause of science but to the larger cause of a forward-looking rational society where scientific outlook is the rule. The process of change can be brought about by altering our method of functioning by infusing scientific methods in administration. She hoped that the seventies would be the decade of decisive development during which the country shall have accomplished economic self-reliance.

The scientists in India do not have the advantages enjoyed by those in the developed countries; they have to work with limited resources, inadequate and sometimes antiquated equipment. Moreover, research institutions suffered from lack of flexibility and certain tasks could not be carried out owing to procedural difficulties. There are unnecessary irritations from the interference of bureaucracy at the headquarters or the Ministries of the Government. Neither we are getting all the returns from our investments nor fully utilizing the talents of our young people. She felt that after a task had been set to a laboratory and the quantum of funds assigned, the laboratory should find it possible to run its own operations without interference from authority.

India's expenditure on scientific research and development had increased in the last 11 years from Rs. 27 crores to Rs. 136 crores and now constitutes about 0.5 per cent of the gross national product and about 3 per cent of the national budget. Though in relative terms the amounts did not seem large, in absolute terms our expenditure on research and development did not compete unfavourably with many of the more advanced countries. Our society

has remained essentially a pre-technological one and unless we accelerate the pace of our social change our scientific activity would remain peripheral and the country might fall further behind. Unless the scientists were conscious of their responsibility to withstand pressures of tradition and hierarchy, they can not forge a truly scientific community. The hierarchy of a scientific community was only to enable it to act purposefully and in unison, not to silence the voice of the dissident or the innovator.

She regretted that in India any pre-project and pre-research discussion was generally absent in scientific laboratories as well as in large technical projects. This was partly because of an apprehension that credit would not be given to the initiator of an idea if he discussed with others, forgetting that the best ideas were those which survived criticism and were sharpened by discussion.

Referring to the import of technology, Smt. Gandhi said that in India import of foreign know-how was unrelated to research and development expenditure. This situation had sometimes led us to buy the same technology several times over, whereas countries like Japan imported foreign know-how through licensing and other agreements but they spent much more on this to develop it further.

She emphasized that it was the ability of our scientists and technologists to develop the country's capability to absorb and improve technology which was relevant to economic growth. The younger generation of scientists would work more readily on new techniques and new-problems, if they were encouraged to take up the problems of research which arose from the needs of industry. Each Government laboratory should function as a research and development organization for a public sector industry, and there should be the closest association between the two.

The outlook of the national laboratories should change. Though objective-oriented research also involved some basic research; they should leave most of the fundamental research to universities, otherwise public sector industries might be tempted to set up their own research and development organization. There is already some pressure in this direction.

Indian Fertilizer Industry

Based on a round table discussion, held in December 1968, the Indian Chemical Manufacturers Association prepared a

blue-print* for the fertilizer industry, whose basic strategy for immediate action was to disengage the linkage of the fertilizer feed-stock programme from the confusing refinery situation and standardize on a series of plants on the basis of unified technology, a balanced order of production-mix for compound fertilizers and a locational disposal around the deficit area.

The 4th plan target of consumptions of fertilizer is 3.73 million tonnes nitrogen and 1.74 tonnes of P_2O_5 . According to the Blue-print, the estimated gap in nitrogen supply in the next five years, viz., 1969-70 to 1973-74, will increase progressively from 1.1 to 1.9 million tonnes respectively and the corresponding P_2O_5 supply gap is estimated at 5000,000 tonnes in 1969-70 progressively going upto 1.2 million tonnes by 1973-74. The total value of imports of nitrogen and P_2O_5 fertilizers in the next five years approximately would be Rs. 1650 crores (assuming N=Rs. 1500/ton and P_2O_5 Rs. 1500/ton).

The blue-print of the ICMA envisages an integrated programme for production of 1 million tonnes of nitrogen and 400,000 tonnes of P_2O_5 in four projects, each for 250,000 te of nitrogen and 100,000 te of P_2O_5 . Each of these projects would have the following plants (tonnes/day): ammonia 1000, urea 1000 and complex 1450, the products would be urea 330,000, complex fertilizer (22.5-22.5-0; 85 per cent water-soluble P_2O_5) 445,000 tonnes. Implementation of this programme would still meet the gap in the capacity that is required to meet our consumption targets. The programme envisaged in the blue-print would, therefore, have to be duplicated in another location in order that we could attain self-sufficiency in nitrogen and P_2O_5 requirements for 1973-74 onwards and increased consumption thereafter.

Feed-stocks for Ammonia: The naphtha production and availability situation indicate clearly that the projected refining capacity by 1973-74 would not allow any further additional naphtha-based capacity that those under production and under construction. The known resources of natural gas in Assam and Gujarat would have been fairly fully utilized by Namrup Expansion, Gujarat State Fertilizer and Kandla projects. The available LSHS (low sulphur heavy stocks) and other heavy residuals from the projected refining capa-

city by 1973-74 would be available for further production of nitrogen by the partial oxidation route, but the total quantity available would not meet the requirements of a 5-million tonnes programme. Further production of nitrogen has, therefore, to be based on other feed-stocks, viz. nuclear power, coal, crude oil, fuel oil and imported ammonia.

After pointing out the economics and the operational problems, the Blue-print points out for basing further capacity of nitrogen on the possible import of crude or fuel oil. The points in favour of crude over the fuel oil are (i) the import of the former would save Rs. 4 millions annually in foreign exchange compared to that of fuel oil, (ii) the total investment of fertilizer programme based on imported crude would cost Rs. 157 millions less compared to imported fuel oil scheme, (iii) the production cost of ammonia would be Rs. 53/te less for a 1000 million tonne plant based on naphtha produced out of crude topping compared to one based on fuel oil, (iv) it would be easier to locate and broad-base crude oil procurement compared to fuel oil since fuel oil source is tied up with the refinery operations. The continuous and steady availability of crude oil is much more ensured compared to fuel oil, which is dependent on refinery throughput and its marketing conditions, etc. (iv) for the present, fuel oil in India is having leviable excise duty amounting to Rs. 90/te. Its exemption for fertilizer use is tied up with other factors and might cover wider field in the industry and might pose difficulty in aiming at a straight forward decision by the Government.

Hence, the 1973-74 programme would have to depend on imported crude. As and when more indigenous crude is available, the import would be substituted. The programme envisages use of 1.2 million tonnes of crude oil for 1 million tonnes of nitrogen programme in a crude topping unit, which will provide straight-run naphtha for feed-stock for one of the four satellite projects (250,000 tonnes of nitrogen) by the steam reformation process and the remaining heavier fraction for three units each of 250,000 tonnes nitrogen by the partial oxidation process. The topping unit will make available additional 122,000 tonnes of straight-run naphtha, which can be used to provide a 600 te/day ammonia production capacity.

As regards the location of the crude topping unit, the Blue-prints suggests a coastal point or on a crude pipeline. The electro-

*The Fertilizer Blue-Print (Indian Chem. Mfg. Assn., Bombay Regional Office), Oct. 1969

thermal phosphorus plant would have to be located at Udaipur-Kota region as a part of the satellite nitrogenous fertilizer units. One of the four projects would be located at the same place as the crude topping unit; three others strategically located from the point of view of market.

Regarding phosphatic fertilizer production, according to the Blue-print, the following choices are available: electrothermal route, use of sulphur for production of phosphoric acid by wet process and nitric acid process wherein sulphur is not required. From the point of view of total cost—both foreign exchange (capital and recurring) and production costs—the practical choice is for the nitric acid route, which can be supplemented by small quantities of electrothermal phosphoric acid for the production of 22.5:22.5:0 type of product with 85 per cent water-soluble phosphate.

The only practical indigenous source of rock phosphate is Udaipur. The phosphate required can be met from the potential Mussoorie rock phosphate deposits through another programme based on nuclear power.

Investment and Sales: The total capital investment for one million tons nitrogen and phosphatic programme would be Rs. 353 crores (excluding working capital) of which foreign exchange required each year for import of 1.25 m. tonnes crude would be Rs. 12 crores. The total sales turnover of products would be Rs. 280 crores (Rs. 20/unit for both nitrogen and P_2O_5). The sales turnover/investment ratio is 0.8.

Progress of Indian Fertilizer Industry

According to Petroleum and Chemicals Ministry's annual report, released recently, 15 factories—8 in public and 7 in private sector—with an installed capacity of 1.344 mil. tonnes for nitrogenous fertilizers were in production. In addition, 8 projects—7 in public and one in private sector—with a total capacity of 1.21 million tonnes of nitrogen were under implementation. Another 12 projects—4 under public or cooperative sector and 8 in private sector—with a total capacity of 2.146 million tonnes, though approved in principle, were not yet firmed up.

Phosphatic fertilizers are produced along with nitrogen fertilizers in most cases. The installed capacity of these fertilizers was 0.412 mil. te. and additional 0.423 mil. te. was under implementation.

At the Sindri factory the need for mineral gypsum is expected to be eliminated by 1971-72 when the rationalizations scheme would have completed. Nangal unit is constantly showing good results and efforts are being here to reduce cost and improve production still further. Considerable progress was attained in diversification of products at Trombay factory, such as liquid carbon dioxide and ammonium bicarbonate, which have already been put in the market, and a carbon black and a concentrated nitric acid plants are under construction. The Gorakhpur and Namrup units went into commercial production in early 1969. Durgapur factory is expected to be completed by September 1970 and Barauni project in 1971-72. Namrup expansion project is expected to go into production during 1971-72 and Trombay expansion using imported ammonia by 1973-74.

Each of the coal-based projects at Talcher, Ramagundam and Korba is likely to cost Rs. 70 crores and is designed to produce 2,28,000 tonnes of nitrogen. While Talcher and Ramagundam projects will be using 9,68,000 tes, Korba will consume 8,35,000 tonnes of coal per annum.

The fertilizer plant at Udyogamandal has completed three stages of expansion and the fourth stage raising the ammonia capacity to 340 tonnes/day and reducing the consumption of electric power is in progress. The Cochin project having a capacity of 1,52,000 tonnes of nitrogen in the form of urea is expected to be completed in the latter half of 1970.

The Madras Fertilizers Ltd., a joint venture of Government of India and M/s Amoco India Ltd., of USA, is likely to go into production in 1970-71. It will manufacture, ammonia, urea and complex fertilizers and will have a capacity of 1,90,000 tonnes of nitrogen and 80,000 tonnes of phosphates.

[*FCI News*, 8(2) (1970), 11]

New Plants at Sindri

In order to improve the efficiency of the existing plants of the fertilizer works at Sindri, the following 3 sections have been added at a cost of Rs. 1.13 crores: naphtha gasification, MEA washing in gas reformation plant and acid neutralization in urea plant.

Naphtha Gasification: Due to deteriorating quality of coal the gases produced in the coke ovens are not adequate to meet the requirements for production of 189 tonnes of ammonia, which was the original capa-

city of the gas reformation plant. So a naphtha reformation section has been installed to produce reformed gas equivalent to 60 tonnes/day of ammonia. This gas will be ultimately mixed up in CO-conversion section of gas reformation plant and processed to produce synthesis mixture for ammonia. The plant will get its requirement of 50 tonnes/day of straight-run naphtha from Barauni refinery.

MEA Washing Section: As the carbon dioxide removal section in gas reformation plant does not have adequate capacity, the consumption of caustic soda increases particularly as more than the required quantity of carbon dioxide escapes from water washing section. So a new unit for carbon dioxide absorption by mono-ethylene-amine has been installed to enable MEA solution (20 per cent) to dissolve carbon dioxide which later on will be evolved on regeneration. This regenerated solution of MEA will be recycled back resulting in the minimum loss of MEA and improvement in the capacity of carbon dioxide removal section.

Acid Neutralization Section: This section has been added to utilize 200 tonnes/day of sulphuric acid being produced. In the original plant tail gas from urea reactors was being absorbed in water and sent back to sulphate plant for production of carbonated liquor. With this new section this tail gas, consisting mostly of ammonia and CO_2 , will be neutralized with sulphuric acid in a saturator. The concentrated ammonium sulphate of 45-48 per cent strength will then be utilized in Double Salt and Sulphate plants. The capacity of this section is 270 tonnes/day equivalent to ammonium sulphate. This section will be beneficial to the double salt plant where Lurgi evaporators were getting fouled due to calcium carbonate coming along with ammonium sulphate liquor from sulphate plant. It will also improve the stream efficiency of urea plant and make it independent from sulphate plant.

The MEA Washing and Acid Neutralizations have been designed by the P & D Division of FCI Ltd.

[*FCI News*, 8 (2) (1970), 16]

Performance of Some FCI Units

The Nangal unit of Fertilizer Corporation of India has established a new record in ammonia production. It produced 323.8 tonnes on November 16 beating previous highest record of 323.31 tonnes. This is much above the rated capacity of 307.2 tonnes/day.

The Gorakhpur unit has exceeded its rated capacity in the production of urea. While its rated capacity is 543.5 metric tonnes/day, the actual production since November 8 to the end of December 1969 ranges from 545 to 600 metric tonnes. This unit went into commercial production in January 1969 and within the first three months of its production ending on March 31, it after providing, for depreciation and interest, made a profit of Rs. 15.07 lakhs. During the year 1969-70, the factory is likely to make a profit of about Rs. 230 lakhs. Efforts are being made to irrigate its 100 acre farm utilizing the factory's effluent and sewage.

The Sindri factory has exceeded its production target. During the year ending on March 31, 1970, it produced 87,306 tonnes of nitrogen—3064 tonnes more than the production target—inclusive of 77,000 tonnes in end-products and 7,242 tonnes by sale of ammonia set for the year. It produced 2,91,000 tonnes of ammonium sulphate, 42,727 tonnes of double salt and 15,738 tonnes of urea. The adding of the two new sections recently, viz. naphtha reformation to produce gas equivalent to 60 tonnes/day of ammonia and an acid neutralization section to utilize 200 tonnes of sulphuric acid obtained from the sulphuric acid plant, was one of the factors for this encouraging performance.

Sindri News, 5 (4) (1969), 12; *FCI News*, 8 (2) (1979), 10]

Oil Price Fixation

The Government of India announced on May 11, 1970 new prices for oil products which will come in force on June 1 and shall remain for 3 years. These will maintain the prices substantially at the existing level except for the refinery towns and neighbouring areas, where the consumers may get some marginal reduction. The cut in the prices would mainly be in freight charges from the new pricing points—Koyali in Gujarat, Gauhati in Assam and Barauni (Bihar). The new price formula provides for a Rs. 10/kilolitre surcharge on all-India basis to meet the losses on under recovery of freight due to fixation of new inland pricing points. The surcharge is expected to yield about Rs. 17 crores, out of which Rs. 12 crores would be disbursed to the companies to meet their under-recovery of freight losses. The rest will go to the Government exchequer in the form of non-recoverable duties. The formula also envisages lowering of marketing charges.

Under the new formula there will be a slight decrease in the price of motor spirit 79, light diesel oil and kerosene. There will be slight rise in the prices of furnace oil, naphtha and motor spirit 93.

The Government decision is based on the recommendations of the Oil Prices committee headed by Sri Shantilal Shah, which submitted its report in November 1969. The spokesman gave some instances: motor

spirit ordinary will come down by Rs. 34/kilolitre in Koyali, inferior kerosene will be cheaper in Koyali by Rs. 32/kilolitre; in Barauni high speed diesel will cost Rs. 47/kilolitre less and light diesel oil Rs. 51/kilolitre less; in Gauhati superior kerosene will be available to the consumer for Rs. 17 less than the existing price. Furnace oil will be available for Rs. 42 less than the existing price. The Government has also accepted the committee's suggestion for the continuance of the concept of import parity in determining the basic ceiling selling prices of petroleum products. Till now, the import parity was based on posted FOB prices of products at Bandar Mah Shahr port in Persian Gulf. Henceforth, however a discount of 4 per cent will be applicable to the posted price, which is calculated on the basis of \$ 1.28/barrel of crude. The committee has recommended that if the discount on light Iranian Agha Jari crudes increases, the discount on the posted prices of products should be increased by 4 per cent for every 10 per cent extra discount on crude. The dealers' commission on motor spirit, high speed diesel and kerosene will remain at the same rates as at present. The Government considers the following recommendation desirable which should be followed up; the entire crude oil imported into the country should be canalized through a single agency. The Government also proposes to set up an expert committee to investigate the cost of indigenous crude.

News in Brief

Ammonia Synthesis in Fluidized Bed

An industrial-sized column has been set up to carry out practical verification of theoretical investigations concerning the production of ammonia using a fluidized bed containing an iron catalyst*. Tests to date have confirmed that in such a bed using a fine-grained granular catalyst more efficient use to be made of the catalyst surface and optimum temperature conditions to prevail, and simplifies column design and construction. The higher efficiency of the column reduces the recycle ratio of the gases in the synthesis loop, which in turn reduces production costs by lowering power consumption.

[*Nitrogen*, No. 58, (1969), 49]

Ammonia Tankers

For ammonia movement between two distant points steel pressure containers of smaller capacity proved too costly mainly because of the immense non-earning weight of the pressurized containers. By 1960 the semi-refrigerated tankers were being built and larger cargoes became feasible. In such tankers, the liquid cargo is carried at a sufficiently low temperature to enable the tank pressure to be kept within practical limits, while the tanks themselves are insulated to reduce the amount of heat ingress to the liquid. The 'boil off' gas, the result of imperfect insulation, can be reliquified and returned to the storage systems. With this method of product storage on board, the possible cargo capacity of LPG/ammonia tankers has expanded considerably and semi-refrigerated tankers are now in operation capable of carrying some 7,500 tonnes of ammonia at more attractive costs from the point of view of both the shipper and the customer. The first refrigerated tankers, specifically designed for ammonia transport, was launched in Holland in 1964, with a view to transport surplus ammonia from Grace facilities in USA and the Trinidad plant of the Grace's subsidiary company to Europe. By the end of 1969 twelve LPG tankers each in excess

of 10,000 tonnes for carrying ammonia should be operating and in France and Italy several tankers to be launched this year will have capacity 27,000 tonnes of ammonia. A notable offshoot of this development has been the gradual entrance of some fertilizer and fertilizer intermediate manufactures into the shipping business.

[*Nitrogen*, No. 58, (1969), 21]

Nitrogen Fertilizer Trade

Against a background of a general further weakening in prices, major world exporters of solid nitrogen fertilizers by and large returned favourable results in 1967/68 and total world exports rose by 13 per cent to 5,366,000 tonnes N, following an increase of 19 per cent in the previous year. Pressures on suppliers continued to intensify as export availability built up throughout the major supply areas and competition in smaller tonnage markets was keen, to the point that requirements tended to be heavily oversubscribed at very low prices.

The most significant development during 1967/68 has been the reassertiveness of E. European suppliers in the developing countries. USSR trade in nitrogen rose by 62 per cent to reach a new peak of 257,000 tonnes N, while E. German trade picked up again after a period of contraction. Rumania, Bulgaria and Poland also registered major expansions in nitrogen exports through extremely competitive sales programmes in a number of major world markets, notably in Asia and Africa. Japan has enhanced its position as leading world exporter by supplying more than 13 per cent more nitrogen, thus passing one million tonnes per year mark. USA again registered a high rate of growth, reflecting the level of procurements of its export products through the AID programme. For W. European suppliers the year was generally satisfactory.

Among the products entering world nitrogen trade, urea, ammonium nitrates and complex fertilizers are the main. Ammonium sulphate trade, having reached a peak of 1.5 million tonnes N in 1966/67, slackened off to 1.4 million in 1967/68,

clearly because of the rise of popularity of urea. Urea exports rose by 36 per cent to 1.75 million tonnes of N, representing one-third of all trade in solid nitrogen fertilizers. The expansion of trade in complex fertilizers confirms trend to high analysis products, as the market expanded by 38 per cent to 873,000 tonnes N, comprising partly in deliveries of ammonium phosphate types and products like 15-15-15, 17-17-17 and 18-18-18.

[*Nitrogen*, No. 58 (1969), 14]

Manure From Tannery Wastes

During the processing of hides in tanneries, a considerable quantity of animal hair becomes available as a waste. Similarly wool waste is available in large quantities. The Indian Agricultural Research Institute has developed a process for the production of rich organic nitrogenous manures from these wastes. It is simple and involves operations like washing, mixing, precipitation, filtration, etc. The manures thus prepared contain 2-15 per cent nitrogen. The chemicals required in the process are caustic soda and hydrochloric acid. The total capital outlay for a plant of 10 tonnes throughout per month of hair has been estimated at Rs. 4000/- The cost of production per tonne comes to Rs. 80/-.

[*Leather Science*, 16 (1969), 276]

North Sea Gas

ICI and Shellstar Ltd. have each signed contracts with the Gas Council of UK for the purchase of North Sea Gas to be used instead of naphtha as feedstock for ammonia production. ICI will use the gas at its Billingham and Severn side plants and is expected to take upto 250 MMcf/d under a 15-year contract (starting from 1972) said to be worth about \$ 600 million.

Shellstar has signed a \$ 19.2 million contract to buy about 35 MMcf/d of gas for its plant under construction at Ince Marshes, Cheshire.

[*Oil Commentary*, 6 (20) (1969), 12]

Petrochemical Complexes in India

M/s Polymer Corpr. of Canada have offered to participate in a study of the

*Anekhin, V. N. et al, *Khim Prom*, (1968), 7, 509.

market for synthetic rubbers in the country in the next 5 to 10 years and the measures to be adopted for the manufacture of the appropriate varieties as part of the Koyali complex. The terms of the offer are under consideration.

A letter of intent has been granted to the Assam Industrial Development Corporation. Ltd. for the establishment of a number of petrochemical units at Moran-Lakwa areas in Sibsagar district of Assam. The items and their production capacities are as follows (capacity in tonnes/annum): methanol 7000, formalin 12,000, non-concentrated glue (50 per cent) 12,000, concentrated glue (75 per cent) 13,000, urea formaldehyde moulding power 1000 and PVC processed goods 6,000.

[*Oil Commentary*, 7 (1) (1969), 11]

Production of Naphtha

The production of naphtha during 1968 was 937,000 tonnes which is expected to increase to over 1 million tonnes during 1969.

[*Oil Commentary*, 7 (1) (1969), 20]

Desert Reclamation

As a result of a successful experiment carried out by the Central Soil Mechanics Research Station (CSMRS) of the Irrigation & Power Ministry of the Government of India, it is now possible to reclaim saline-alkaline areas of Rajasthan desert, declared unfit by foreign experts. The FAO, UN Development Programme and Central and State Government agencies after carrying out detailed soil survey of about 10,000 acres in the Anupagarh Shakha branch of Rajasthan canal had come to the above conclusion and it had been thought that the water provided by the distributory of the canal would go waste.

On the basis of the results of the tests carried out, different plots were prepared giving different treatments which included flooding with water using gypsum, ploughing the fields, growing 'dhaincha' (green manure) and ploughing it back into the soil, etc. When it was found that this was low enough to grow a crop, rice cultivation was undertaken with the application of farmyard manure and chemical fertilizers. The result was a bumper crop of 60-70 maunds of rice per acre where not even a blade of grass grew. The crop is to be cut at the end of October and the scientists at the research station say that the yield compares more than favourably with a good rice crop elsewhere, particularly with the best farm in the region.

Liquid Ammonia Pipeline

Investigations by the Centre's team of experts into the Assam's demand for a second public sector refinery have led to suggestion for distribution of liquid ammonia by pipeline from Assam to Delhi. The experts committee is of the opinion that Assam crudes, rich in aromatics, has scope for an integrated production of aromatics, ammonia, petrochemicals by their direct conversion into chemicals. They also feel that the Ganga basin can absorb large quantities of fertilizers and by 1973-74 there would be a shortage of 300,000 tonnes of nitrogenous fertilizers. The liquid ammonia can be converted into fertilizer salts in plants in each agricultural region. They have advised production of ethylene and higher gaseous olefines along with the production of aromatics and ammonia. According to them, it would also be desirable to include a polyester plant to produce nylon and manufacture of benzene and cyclohexene.

[*FAI Inf. Serv.*, 10 (21) (1969), 7]

Ammonia Storage

A horton sphere, measuring 17000 mm. diameter for the Barauni unit of FCI Ltd., is nearing completion at the Heavy Machine Building plant of the HEC Ltd, Ranchi. It will weigh 180 tonnes and 256 tonnes including supports and auxiliary structures. The entire design and technology in its manufacture as well as jigs and fixture required for the job was done for the first time by the HMBP itself. The sphere can hold 1500 tonnes of liquid ammonia at -20°C at 3.5 kg/cm^2 ; boiler quality steel plates have been used and the double curvature spherical bending has been done in the plate banding machine. There is an order for one more sphere—125000 mm. diameter for storage of liquid petroleum gas to be installed at Bombay for M/s Burmah Shell.

[*Lok Udyog*, 3 (7) (1969), 790]

ICI Methanol Process

ICI's low pressure methanol process has now been adopted for 4 plants to be built in different parts of the world to produce a total of 800,000 short ton/year. The latest of these is a 100 short ton/day single stream unit which will be built by Chemico for the Monsanto Co. This process has been licensed by ICI to Chemico, Humphreys & Glasgow, Kellogg, Power Gas and Uhde.

A copper-based catalyst, manufactured by ICI and Katalco Corpr, permits methanol synthesis at 750 lb/sq.in. and below 300°C compared to the conventional high pressure process which requires pressures upto 5000 lb/sq.in. and temperature $300-400^{\circ}\text{C}$. The operating conditions using this catalyst result in low by-product formation and lower power requirements, thereby reducing operating costs. Capital costs using low-pressure process for both large and small plants are more favourable than those for the conventional process.

[*Chem. and Indus.*, No. 11, (1969), 304]

Ammonia Plants

Ammonia production during the post-war years is characterized by a steady uniform growth devoid of wide fluctuations. Since 1960 the production of nitrogen has increased by 2 million tons/yr, in 1966 the same increased to 2.7 million tons and reached a total of 26 millions; the main participants in this production are as follows: W. Europe 8 millions, USA 7.5, E. Europe 5 and Asiatic states 4 millions half of which is concentrated in Japan. Japan takes the first place among the world ammonia producers. To accelerate the growth of agriculture, developing countries like India, Pakistan, UAR, Mexico, Colombia, Greece, Argentina Australia and others are building ammonia plants.

As regards capacities, the most frequent are 30,000 and 40,000 tons NH_3 /yr, the number of which is 25 out of 318 operating plants (on 1.3.68). The next most used plants are those having capacity of 100,000 tons NH_3 p.a. Apart from these, there is an average of 10 plants on stream for each of the capacities 50, 60, 70, 80, 90, 120, 130, 180 and 200 thousand tons p.a. Plants with high capacity, say 300,000 t, have been brought into operation recently; there are now 16 such plants on stream and are mostly in single-train with lower synthesis pressure (150-200 atp) employing turbo-compressors. Plants having capacities greater than 300,000 t are very few—not more than 13.

The modern trend is of increasing capacities. The producers are now offering units with 1500 or 200 t/day output. The American branch office of Haldor Topsoe has proposed an output of 3000 tons/d of ammonia, using turbo-compressors operating at 280 atm. Research workers in USSR, Switzerland and USA are investigating new ammonia processes which promise to eliminate high pressure and temperatures

—nitrogen with dicyclopentadienylniobium dichloride in presence of ethylmagnesium halide at room temperature and atmospheric pressure can be converted to ammonia. Another discovery is formation of a stable complex with ruthenium, rhodium and iridium by nitrogen.

[*Brit. Chem. Engng*, **14** (1969), 813]

Patents*

Ammonia Synthesis: R. A. McCallister and A. M. Sinclair (to Foster Wheeler Corp.), U.S. 3,432,265, Mar. 11, 1969, Appl. Apr. 13, 1967; 6 pp.

A process is described in which partial oxidation of a hydrocarbon is obtained by contact with steam and H yielding a gas stream comprised of H and CO with traces of CO₂ and CH₄. This stream is passed through a catalytic shift conversion unit in which the CO reacts with steam to form additional H and CO₂. The gas stream is then passed through scrubbers to remove CO₂ and then CO. N is added to the scrubbed mixture in the amount required for NH₃ synthesis, and the mixture is passed through a catalytic NH₃ synthesis converter. A waste heat vapor generator is utilized whereby superheated steam is generated for direct use in the partial oxidation cycle. Heat usually lost is returned to the vapor generator for combustion. Thus, the fuel oil and C usually exhausted after the partial oxidation and the waste gases usually exhausted during CO₂ removal, CO removal, and NH₃ synthesis, are sent to the combustion section of the waste heat vapor generator.

[*Fertilizer Abstracts*, **2** (6) (1969, 17)]

Removal of Carbon Dioxide and Hydrogen Sulfide from Gases: C. S. Smith (to Chevron Research Co.), U.S. 3,435,590, April 1, 1969, Appl. Sept. 1, 1967; 7pp.

Liquid propylene carbonate, Me₂CO, or MeOH (I) is used as absorbent to remove CO₂ and/or H₂S from H-containing gas mixtures, for example, in purifying H produced from CH₄ by steam reforming and shift conversion. Cold lean absorbent, such as, I at—90°F. is fed to an intermediate point in a bubble-cap absorber column and flows downward in countercurrent contact with the gas mixture. The gas containing

H 60, CO₂ 25, CO 2, and H₂S 2 per cent, is fed to the base of the column at 100°F. and 250-1500 psia. Contact with the cold I in the absorber cools the gas, which is then contacted with a stream of warm (80°F) I fed to an upper part of the column thereby cooling the I and warming the gas. The gas is then washed with H₂O in the top of the column; the aqueous wash liquor is withdrawn separately, and purified H leaves the top of the column at 70°F. Optionally, the gas is warmed to only 35°F. by contact with the warm I, in which case the H₂O wash can be eliminated or reduced. This is desirable if the gas is to be subsequently treated for CO removal by absorption in refrigerated cuprous ammonium acetate. The absorbed CO₂ and H₂S is much more soluble than CO₂ in I they can be recovered separately. The equipment is smaller and less expensive than that required in usual processes because the heat exchange is by direct gas to liquid contact instead of the usual indirect gas to gas heat exchange.

[*Ibid*]

Fertilizer from Phosphate Rock and Basic Slag: Societe Financiere et Industrielle D'Egypte S.A.E. (by Mohamed Shafik and Abdel Fattah Sabry). Brit. 1,146,970 Mar. 26, 1969, Appl. Dec. 12, 1966; 4 pp.

Phosphate rock is treated with HCl and the resulting H₃PO₄ neutralized with basic slag. Preferred conditions are (1) 35-50 parts by wt of acid/100 of phosphate, (2) treatment at a temperature between 75° and boiling temperature, (3) treatment period of 0.5-15 minutes, and (4) filtration of the H₃PO₄ before neutralization. A typical product contains 29.06 per cent P₂O₅ of which 79.7 per cent is citrate soluble.

[*ibid*]

Recovering Phosphorus from Sludge: J. A. Hinkebein (to Monsanto Co.), U.S. 3,436,184, Apr. 1, 1969, Appl. Aug. 25, 1964; 7 pp.

Addition of an H₂O-soluble inorganic hexavalent oxy-chromium compound to sludge formed in a P condenser sump causes the P to settle to the bottom in a coalesced layer. Thus, sludge decanted from a P condenser sump containing 34 per cent liquid P, 13 per cent solids, and 53 per cent H₂O was fed at 45 gal/hour to a mixing tank stirred with a blade rotating at 105 rpm. An aqueous 1 per cent CrO₃ solution was also fed to the tank at 90 gal/hour. The treated sludge containing 4.66 per cent P and 89.73 per cent H₂O was continuously withdrawn as overflow. Liquid P containing 0.29 per cent CrO₃ and

0.005 per cent benzene-insoluble matter was withdrawn from the bottom of the tank. Optionally, the CrO₃ can be added to the condenser H₂O.

[*ibid*]

Separating Phosphorus from Gas Streams: H. M. Stevens (to Monsanto Co.), U.S. 3,433,601, Mar. 18, 1969, Appl. Oct. 7, 1965; 4 pp.

Elemental P is recovered from reduction furnace gases by cooling the mixture to a temperature below the dew point but above the melting point of P (60-180°C). The P is thereby condensed and collects in liquid form. The liquid P is maintained in turbulent flow by recirculation to prevent sedimentation of solid impurities in the condenser and piping. Cooling is by indirect heat exchange with air or water. The method avoids the problems of "phossy water" and sludge in the usual wet method of condensing and collecting P.

[*ibid*]

Antifoam Agent for Phosphoric Acid Manufacture: G. E. Dorwart (to Betz Labs. Inc.), U.S. 3,437,437, Apr. 8, 1969, Appl. Oct. 5, 1966; 6 pp.

The title products are prepared by reacting and hydroxyl amine with a fatty acid such as those present in tall oil heads. Thus, 227 parts (wt) tall oil heads (containing oleic acid 33, linoleic acid 24, and stearic acid 25 per cent) preheated to 150°F. was charged to a vacuum reactor. Then 23 parts diethanolamine was added and the mixture was rapidly heated to 400°F. while pressure was reduced to 23 mm Hg. The reaction was continued until an acid value of 16 was obtained (theoretical for the formation of the diester) which required five hours. The reaction mixture was cooled to 190°F and removed from the reactor. Such products control foaming in the manufacture of H₃PO₄ by the wet process. The dosage is 0.1-5 lb/ton phosphate rock.

[*ibid*]

Water-Soluble Polyphosphates: G. Ewart and J. S. Raitt (to Scottish Agr. Ind. Ltd.), U.S. 3,432,261, Mar. 11, 1969, Brit. Appl. Mar. 25, 1965; 3 pp.

Novel H₂O-soluble chain polymer polyphosphates having high Ca-sequestering power are made by boiling crude KPO₄ with an aqueous solution of NaCl or NH₄Cl. The resulting solution is filtered, and the filtrate is cooled and treated with acetone whereby a precipitate of Na-K-polyphos-

*These patents have been reproduced from Fertilizer Abstracts published by the National Fertilizer Development Centre, TVA, Muscle Shoals, Alabama, USA with kind permission of the Editor FA.—Editor

sulphur, such as anhydrite, gypsum and phospho-gypsum, are also discussed.

The process problems and maintenance difficulties encountered in operating a 165 tonnes/day phosphoric acid plant, the remedial measures taken and also special provisions made while locating phosphoric acid plant at Baroda are discussed in a paper.⁷

For setting up phosphoric acid plants the lion's share in the investment is spent on foreign exchange as most of the materials and equipments have to be imported. The materials of construction in phosphoric acid plants with special reference to those adopting wet processes and the extent to which import substitution could be done have been discussed. It has been possible for FACT Engineering and Design Organization⁸ to design a 360 tonnes/day phosphoric acid plant using the central Prayon Hemihydrate process with a total foreign exchange requirement of Rs. 10 million out of the total installed cost of Rs. 30 million for the entire plant.

The operation of a Prayon multi-tank type phosphoric acid plant at Ennore with a capacity of 32 tonnes/day has been described⁹ by R. S. Raman (EID-Parry). The effect of the various impurities in the rock phosphate, the different factors affecting efficiency of extraction and filtration of phosphoric acid and the means of control of the factors are discussed. The materials of construction employed with corrosion problem, disposal of wastes and attempts made at the plant for import substitution are described.

In the paper, 'By-product Gypsums for Ammonium Sulphate Manufacture', by V. A. Sanghani and Kumar Desai (GSFC), details of experience gained in the operation of an ammonium sulphate plant based on phospho-gypsum are given. This process is important for countries with no sources of sulphur. There are proven processes for converting gypsum into sulphuric acid or ammonium sulphate; however, the cost of conversion to former is very high and involves huge capital investment. To make phospho-gypsum conversion to ammonium sulphate economically attractive, adequate care has to be taken in the production of phosphoric acid and good quality gypsum.

The operational difficulties of phosphoric acid plant of the Gujarat State Fertilizers Co.Ltd. at Baroda have

been discussed¹⁰ with suggestions to overcome them.

The following are the suggestions and recommendations made by the seminar for consideration by the industry.

Phosphate Rock: In order to enable the superphosphate industry to improve its competitive position *vis-a-vis* high analysis phosphatic fertilizer now available in India as also to economize on freight and transport charge it is desirable that only high grade phosphate rock should be imported. The analysis of the rock required by the phosphoric acid industry should conform to the specific requirements of the plants.

The commercial supply of indigenous phosphate rock should be rapidly organized and developed on scientific lines so as to provide increasing quantities of rock of standardized quality to the industry.

Rehabilitation of the Superphosphate Industry: It is in the national interest that the single superphosphate industry whose numerous units are dispersed over the country and in which a substantial amount of capital has been invested should be enabled to hold its own and make a full contribution to the total supply of phosphatic fertilizer in the country. For this purpose, the industry should be helped to upgrade its basic products by compounding them with high analysis intermediates and fertilizers, such as ammonia, phosphoric acid, mono-ammonium phosphate, diammonium phosphate, urea, and potassic salts. Indigenous research and experience abroad have shown the technical feasibility of producing granulated high analysis compounds based on purer phosphate. To make such products economically competitive, it is essential that the material required should be supplied (if necessary, by importing them) to superphosphate manufacturers at bulk rates.

Changing Pattern of Fertilizer Movements: The Railway Board should be invited to take note of the changes taking place in fertilizer movements. The rapidly increasing quantities of fertilizers produced and imported make it necessary for the railways to accept fertilizer in bulk or packed in non-jute materials for transport; this will help to conserve the supplies of jute for the transport of agricultural produce. The likely production and import of ammonia and phosphoric acid in the future will call for the provision of special tank wagons for their internal transport. It is desirable that the Railway Board should revise its goods tariff suitably and plan for the creation of facilities for the movement of ammo-

⁷ Process Difficulties and Maintenance Problems of Phosphoric Acid Plants by V. A. Sanghani and S. K. Grover (GSFC).

⁸ Materials of Construction and Import Substitution in Phosphoric Acid Plants.

⁹ Case Study of Operation of Phosphoric Acid Plant.

¹⁰ Technology and Operation of Phosphoric Acid Plants by L. Singh (GSFC).

nia and phosphoric acid in consultation with the industry.

Import Substitution: While the need for import substitution and indigenisation of equipment and raw materials in the fertilizer industry is fully recognized, it is desirable that production is not sacrificed in the short term in the pursuit of the inevitable time-consuming process of import substitution. A balance should be struck progressively between these two desirable objectives in the best national interests.

Plant Maintenance: The crucial importance of plant

maintenance in fertilizer factories in maximizing stream factors was brought out in the seminar discussions. It is recommended that regular meetings of maintenance personnel should be arranged to cover specific areas of operation under the auspices of the fertilizer institute.

The seminar noted the present inadequacy of training facilities for maintenance workers. It is recommended that training of such personnel should be organized as a joint exercise or at the unit level.

[Benoy K. Banerjee]

Notes & News

The World's Largest Coal Based Fertilizer Plant

The foundation-stone for 900 tonnes of ammonia and 1500 tonnes of urea per day capacity coal-based Talcher Fertilizer Project was laid on Feb. 3, 1970 by Dr. Triguna Sen, Union Minister for Petroleum & Chemicals, Mines and Metals. Talcher is located in Dhenkanal district of Orissa and a 250 MW power station of the Orissa State Electricity Board and a well developed coal-mining centre owned by National Coal Development Corporation are already in existence in Talcher. Talcher coalfields consist mainly of two seams, the top and the bottom. This ammonia plant will utilize about a million tonnes of coal per year entirely from the bottom seam of South Balanda mines, reserves of which are estimated at about 27 million tonnes. The total water requirement for both process and sanitary purposes including the use of some raw water for ash disposal will be about 15 mgd. This water requirement will be met from river *Brahmani*. Total investment is to the tune of Rs. 70.5 crores of which Rs. 20 crores will be in foreign exchange. The return on capital will be about 16 per cent. The payback period for the project is 4.1 years. When plant goes

on stream it will save Rs. 36.48 crores per year foreign exchange due to reduction in import of fertilizers and will employ about 1200 skilled workers. The design and engineering of the project will be done by the Planning & Development Division of Fertilizer Corporation of India Ltd.

When good quality Talcher coal to feed any industrial plant was discovered, tests were conducted at the Central Fuel Research Institute, Dhanbad and National Metallurgical Laboratory, Jamshedpur. The former recommended the establishment of an industrial complex based on Talcher coal. A detailed project on an LTC plant (coke being utilized for pig iron manufacture and LTC gas for production of fertilizer) was submitted in January 1966 by the Industrial Development Corporation of the Orissa State Government with the help of the Planning & Development Division of FCI Ltd. The scheme was accepted by the Central Government in principle. However, due to several unavoidable reasons, the implementation of this project was postponed. A feasibility report on the establishment of a large coal-based fertilizer plant was prepared as an alternative to the above project on request from the Orissa State Government and submitted in July 1968, and a revised report subsequently in the early part of 1969.

Sri Satish Chandra, Managing Director of FCI Ltd., in his speech at the foundation-stone laying ceremony said "the largest single train coal gasification units on which experience is available is one equivalent to 300 tonnes per day of ammonia. For our 900 tonnes per day ammonia plant therefore we will use three streams at a time. The gases from the three gasification units will then be treated together and synthesized in a large-sized ammonia synthesis unit to achieve economies of scale and to cut down production costs. The urea plants will also be large sized one. The fact that each one of these projects is located almost at a coal pit-head, and that coal will be transported by conveyor belts, and not railway wagons, will also keep costs under control.

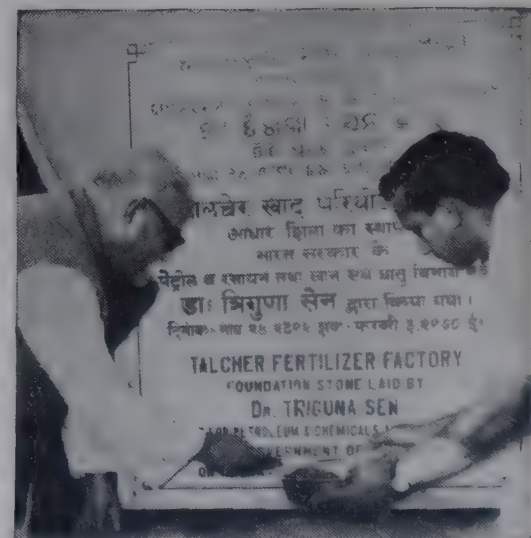
In our feasibility studies, we have made our profitability calculations on the basis

of 330 operating days per year. However, expert opinion has been expressed that no unit can operate for more than 250-300 days. In order not to take any risks and to assure the operability of the plant for 330 days every year we are providing for a fourth gasification unit as a standby. Instead of 3x330 i.e. 990 stream days we shall have 4x250 i.e. 1000 stream days, allowing for downtime of 115 days per year for each unit. This will increase cost but provide greater flexibility and efficiency".

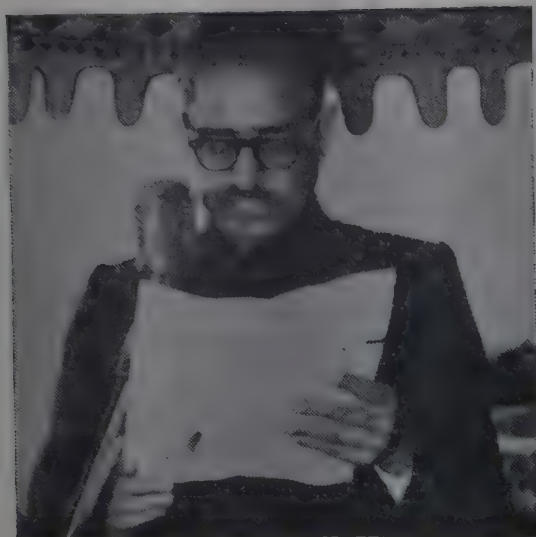
Dr. Triguna Sen in his talk said, "Assured availability of raw material on the spot involving no transportation by rail, as also the availability of important utilities like water and power on the spot do constitute the *sine qua non* for location of plants like this". He maintained that according to experts the cost of production for urea would be only Rs. 340/ton in the coal-based plant, as against Rs. 370/- as naphtha-based plant or Rs. 419/ton as LSHS based plant which has reassured the Government for making a higher investment. The project is expected to be completed within 36 months. i.e. by 1972 and its marketing area will be predominantly the state of Orissa.



Sri R. N. Singh Deo, Chief Minister of Orissa, Delivering the Presidential Speech before the Laying of the Foundation Stone of Talcher Fertilizer Plant



Dr. Triguna Sen, Minister for Petroleum & Chemicals, Govt. of India, Lays the Foundation Stone on Feb. 3, 1970



Dr. K. R. Chakravorty, Director (Tech.) FCI Ltd., Proposes a Vote of thanks

New Ammonium Nitrate Additive

Traditional problems associated with production, use and storage of ammonium nitrate are those of prill break-up and cakings caused respectively by change in crystalline form with temperature alterations and by the constant process of solution and recrystallization of fine particles of ammonium nitrate in absorbed moisture. A recent development in overcoming these problems by Mississippi Chemical Corpr. of USA is an additive known as Permalene-34 for use as stabilizing agent in ammonium nitrate production. The incorporation of this additive into the product fundamentally changes the effect of temperature on crystallographic structure and therefore prill break-up is substantially reduced. Normally there are three temperature-dependent crystalline transitions involving volume change (%) of -2.1 , $+1.3$, -3.6 occurring at transition temperature 125° , 84° and 32°C respectively. Because of expansion and contraction of prills in these three phases its strength is lowered. Besides this in normal storage, ammonium nitrate prills may be subjected to several temperature fluctuations around the 32°C transition point which gives rise to the greatest change in volume and therefore causes considerable prill break-up. This new additive allows only two of these three temperature transitions to occur and alters the temperature at which the other volume changes appear. The 84°C transition no longer occurs at all, the normal 125°C transition at 124°C and most important the usual 32°C transition occurs at 43°C , in most instances a temperature high enough to eliminate the possibility of solid phase volume changes during storage. The over-

all effect is a substantial increase in prill strength which tends to a considerably reduced degree of prill breaking-up during handling and storage.

Apart from avoiding prill break-up during storage by raising the transition temperature, a reduction of the internal stresses in the prill during the transition is also obtained, since this transition takes place over a fairly wide temperature range. In the tests carried out prills containing Permalene-34 withstood thirty transitions between 0 and 60°C without cracking. Because of the change in the lower transition point from 32 to 43°C when using the additive performance of the prills during temperature cycles around 32°C was excellent. Permalene-34 is also reported to reduce caking by decreasing the rate of moisture absorption. It has been stated that this new additive contains nitrogen, but it is not known whether this nitrogen is in active form.

The equipment necessary for the installation of a treatment units consists chiefly of storage, tankage, pumps, piping and instrumentation. Where a complete unit is to be built, Humphreys and Glasgow Ltd. of London, acting as agent for the product throughout the world excluding USA, Canada and N. America, estimate that an additive facility for a 1000 tpd ammonium nitrate plant would involve a total investment cost of about \$ 85,000. Royalties for the process are payable at the rate of \$ 0.30 per short ton of produced ammonium nitrate (i.e. around \$,90,000 per annum for a 1000 tpd plant) and these payments represent one of the largest items in the operating cost.

[Nitrogen, No. 59 (1969), 46]

Reuse of Phossy Water

Reuse of waste water from chemical plants is desirable for several reasons. Various methods were investigated for treating phossy water wastes. One of them used combination of clarification, screening and chlorination of the phossy water wastes to eliminate the elemental phosphorus content, as this method required accurate chlorination control which was found to be impractical. In another method oxidation of phosphorus in the phossy water waste with air was investigated. Neither the time of aeration nor the volume of air used seemed to affect the extent of oxidation and the large amount of unoxidized phosphorus left. However, baffles installed at the settling pond outlet to increase turbulence and aeration of the effluent water decreased the elemental

phosphorus content of the settling pond effluent about 40 per cent. The removal of colloidal phosphorus in the water by filtering would require a filter medium with extremely small pore openings. The large volume of phossy water waste made this method of treatment impractical.

The studies were undertaken at TVA to investigate the reuse of phossy water in the phosphorus production process and thereby to eliminate the need to discharge the waste. The studies led to installing a system for collecting, clarifying and reusing the phossy water in the production process.

Phossy water is collected in sumps at four locations in the phosphorus production facility. Water is pumped from these sumps to storage tank where it is continuously recirculated to present settling, and a stream of the recirculating water is fed to clarifier to remove suspended solids. A flocculating agent is added to water at the clarifier inlet. Magnifloc 521 C (40 ppm) flocculant was found more effective than animal glue.

TABLE—THE OPERATING DATA FOR PHOSSY WATER TREATING SYSTEM

Phossy water to clarifier	
Rate, gal./min.	99
Suspended solids content, ppm	3900
Tons/day	2.6
Phosphorus in water, tons/day	1.0
Clarified Water	
Rate gal./min.	97
Suspended solids content ppm	490
Tons/day	0.2
Solids recovered, tons/day	2.4

The clarifier removes about 92 per cent of the suspended solids in the phossy water and removes about 93 per cent of phosphorus.

The clarified water is stored in tanks and reused in the various parts of the plants where it is needed. Dissolved salts accumulate so that the recirculating water contains about 17 g./l. of P_2O_5 ; 9 g./l. of ammonium expressed as ammonia, and 10 g./l. of fluoride, expressed as F. The concentration of dissolved materials in circulating water is kept from reacting higher values by taking off some of the clarified water. Most of the water bled off is used to slurry precipitator dust. In all, about 6 per cent of the clarified water is drawn off for dissolved solids control. Make-up water for the system comes from various sources. Some of the water present

in the furnace gases as vapour condenses with the phosphorus. Water gets into system when phosphorus or phosphorus sludge is heated in tanks with steam spargers. Fresh water is used to wash phosphorus in tank cars, so the effluents from car washing contributes to the make-up water for the system. Rain water also contributes to the make-up water. Addition of water is usually not required. Nearly all the phosphorus in the phosphy water comes down with solids in the clarifier and is removed in the underflow. The solids contain about 40 per cent phosphorus on a dry basis. The underflow is centrifuged and about 79 per cent of the phosphorus in the underflow is recovered for fertilizer use. The waste material from the centrifuge is a slurry consisting of water, solids and unrecovered phosphorus. This material goes to a tank for settling. The supernatant water is put back into the phosphy water system and the settled solids are burnt to produce impure phosphoric acid.

[*Chem. Engng Prog.*, 65 (6) (1969), 73]

Modern Production of Sulphuric Acid

With the conventional contact sulphuric acid plants, the distribution and heat exchange systems have been improved by gradual evolution so that a standard converter can be designed to give 98 per cent overall conversion on practically any gas. The amount of catalyst required goes up from about 180 l./d. ton of acid for a sulphur burning plant to 250-300 l., with a plant using a dilute SO_2 gas like that from an anhydrite kiln or from some sulphide ores.

Vanadium catalyst do not work below 420-430°C, so to get conversions higher than 98 per cent the reaction equilibrium has to be shifted to the right by removing some of the SO_3 , which is done in the Bayer double catalysis system. In this system, partly converted gas is taken out after the third catalyst bed, cooled in a heat exchanger, passed through an absorber where sulphur trioxide is absorbed in sulphuric acid, heated up again in heat exchangers and finally passed over the fourth catalyst bed. With this arrangement one can convert sulphur dioxide to trioxide with an efficiency of over 99.5 per cent. The extra sulphuric acid yield does not usually pay for the cost of extra absorber and extra heat exchangers in the double catalysis system, but double catalysis is often worthwhile to reduce atmospheric pollution. Under license from Bayer, Lurgi have engineered double catalysis system.

Anhydrite Process: There has been a revived interest in anhydrite plants. Basically the Muller-Kuhne process for making sulphuric acid and cement from anhydrite has not changed much since it was first developed in Germany in 1914-18. The cement is rather like an ordinary dry process cement plant, except that the calcium carbonate is replaced by anhydrite and coke and the ratio of carbon to calcium sulphate and also the atmosphere in the kiln must be closely controlled. This is to ensure that over 97 per cent of the sulphur is evolved and no excessive amount of calcium sulphate or calcium sulphide are left in the cement clinker.

The acid plant can be taken as a typical plant for making sulphuric acid from a hot dirty gas. About 99 per cent of the dust is removed from the gas in a dedusting plant, which consists of a settling chamber, cyclones and dry electrostatic precipitators. This dust is returned to the kilns. If the kiln burden has an excessive concentration of alkali, thick rings in the kiln are formed. The dedusted gas is cooled down with sprays of cold weak acid in a wash tower to 50°C and then indirectly by gas coolers. In the next stage, the mist in the gas is removed electrostatically. Air is added to provide oxygen for oxidizing sulphur dioxide to trioxide. The air-gas mixture is dried in a ceramics packed drying tower irrigated with sulphuric acid. The dry gases are blown through the contact plant, which consists of conventional Lurgi catalyst units with 4 layers of catalyst each. The gas is cooled after each catalyst bed by heat exchangers which heat up the cold incoming gas. The gas leaving the absorption towers of an anhydrite plant is always misty due to the presence of oxides of nitrogen which can be removed by electrostatic precipitators.

Iron Pyrites: Fluid bed roaster, which has the advantage of being good for raising steam as well as having a high throughput, is used for roasting pyrites. Montecatini take the ferric oxide from the roaster and give it a reducing roast to magnetite, which is separated magnetically and reroasted under oxidizing conditions to make it valuable as a blast-furnace feed.

Russians have developed a process, wherein pyrites is oxidized by hot ferric oxide in the absence of air producing a pure sulphur dioxide gas-steam which can be cleaned and converted in a sulphuric acid plant which is much smaller than the conventional plant. The magnetite is

oxidized back to ferric oxide by air in a separate reaction.

Russians have developed condensation-absorption system, in which sulphur trioxide gases from a contact plant are condensed and converted to sulphuric acid in a tower which is cooled by injecting water and cool acid into it. By carefully controlling the conditions of condensation, it is possible to use quite small equipment and still produce sulphuric acid in large droplets. With such equipment the gas-cleaning plant can be simplified.

[*Brit. Chem. Engng*, 14 (1969), 795]

Nitrogen Industries in E. Europe

The nitrogenous fertilizers industry in E. Europe has expanded more than three times during 1960 to 1967, reaching just under 5.5 million tonnes of nitrogen. While almost 69 per cent of this production is attributable to USSR, other countries, notably Bulgaria, Poland and Rumania, have also expanded very rapidly and are now competing successfully on export markets.

Bulgaria: While Bulgarian nitrogen industry was based coal/lignite, discovery of large deposits of natural gas at Tchiren and crude oil reserves at Tyulenovo, Gigen and most promising Dolni Dubuik has prompted a mass change in the use of raw materials as well as expansion of the industry. A 435 miles pipeline between Izmail (Ukraine) to Bulgaria and Rumania will be operating in 1972 for supplying natural gas. At Dimitrograd and Stara Zagora high grade ammonium nitrates, CAN, urea, ureaformaldehyde resins, and sodium nitrate are being produced. In addition, there are 2 smaller plants—one producing by-product ammonium sulphate and the other at Dryanovo producing ammonium chloride. Until 1967 ammonium nitrate was the main nitrogenous fertilizer exported by Bulgaria mainly to E. European countries. From then onwards it started exporting into markets so far dominated by W. European producers, Japan and USA. The complex at Varna is scheduled to produce 850 tpd of ammonium sulphate and 2500 tpd of complex fertilizers from 1970.

Poland: Although established as far back as World War I, the nitrogen industry was built through successive 5-year plans after the Second World War. It is now the second largest producer in E. Europe after USSR. The sole surviving pre-1920 plant at Chorzow produces 53,000 tNpa of

ammonia from natural gas, the end products being CAN and calcium cyanamide. The Tarnow complex, which began in 1929, has now an output of 275,000 tNpa ammonia, which is processed into ammonium nitrate, urea, calcium nitrate and calcium cyanamide and also other chemicals, like acrylonitrile, caprolactain and by-product ammonium sulphate. The Kedzierzyn plant at Opole, based on coke oven gas, has a capacity around 300,000 tNpa and produces ammonium nitrate and urea. It will very soon start utilizing natural gas. Smaller plants producing ammonia or its derivatives are situated at Ozwiecim and Knuruow, whereas by-product ammonium sulphate plants are in operation at Nova Huta, Czestochowa and Laziska.

Traditionally relying on brown coal, lignite, etc., Poland is now shifting to natural gas and crude oil for a source of hydrogen. Natural gasfields are in the Carpathian foothills, but a large proportion of gas and oil are supplied by Ukraine-Silesia and Friendship pipeline from USSR. The giant complex Pulawy (I and II) in Lublin is based upon Soviet natural gas and associated facilities in section I for production of 1500 tpd of urea with additional 1000 and 600 tpd of urea and ammonia respectively and 3345 tpd of ammonium nitrate, 1500 and 2700 tpd of ammonia and nitric acid and recently urea in section II. In 1968 759,000 te of nitrogen was produced at Pulawy. Poland is exporting fertilizers to W. Germany, Yugoslavia, Czechoslovakia, India, Pakistan, Greece, Hungary, Guinea, Ecqador, etc. The new projects under installation are at Brzezine (Wloclawek) and Bydgoszcz; the former with a primary capacity of 1500 tpd ammonia based on natural gas will produce nitric acid, aqua ammonia and ammonium nitrate. Another large complex has been planned at Police near Szczecin, initially with a capacity of 140,000 t./P₂O₅ p.a. as triple superphosphate, but by 1972 an ammonium phosphate-based NPK unit will be operating with a capacity 900,000 tpa complex fertilizer (8-24-24).

Rumania: It is the third largest manufacturer in E. European of nitrogen fertilizers, mostly based on natural gas and oils located principally in Transylvanian plateau and Muntenia. Much of it destroyed during World War II, Rumania's chemical industry was rebuilt and expanded during successive socialist development plans. The plant at Fagaras has been rebuilt and expanded to the present capacity of 66,000 tNpa producing ammonium nitrates. The plant at Victoria has a capacity around 15,000 tNpa

manufacturing ammonium nitrate. The first large-scale plant (capacity 143,000 tpa) was brought into stream in 1963 at Piatra Neamt with aid and equipment from USSR. It now produces 210,000 and 20,000 tpa of ammonium nitrate and urea respectively based on natural gas and is now slated for doubling of ammonia capacity.

A large complex producing around 200,000 tpa ammonia using natural gas came into operation in 1964 at Turnu Magurele. Besides producing ammonium nitrate (115,000 tpa) and urea (200,000 tpa), there are facilities for production of two grades of diammonium phosphates. A new expansion of this plant has brought its total ammonia capacity to over 500,000 tpa, adding 297,000 tpa urea and 297,000 tpa of nitrate.

A third complex of ammonia capacity 200,000 tpa started operation at Craiora using natural gas. Its end-products include 300,000 tpa of ammonium nitrate and 100,000 tpa urea. The design for the ammonia, nitric acid and nitrate plants originated from USSR while the urea plant using Stamicarbon process was constructed by Friedrich Uhde of W. Germany. This plant has been recently expanded.

The latest plant is at Tirgu Mures using Transylvanian plateau natural gas which started producing in 1966 90,000 tpa ammonia by the Montecatini process, its principal end-product being 34 per cent ammonium nitrate. The second stage of this plant, already completed its trial run, comprises additional production of 100,000 and 300,000 tpa of ammonia and nitrate.

The above three E. European countries represent a considerable and growing force on the world nitrogen export market and represent the greatest competitive threat to the established nitrogen exports of W. Europe.

[*Nitrogen*, No. 59, (1969), 18]

Synthesis Pressure for Large Ammonia Plants

Most plants built during the past four years have been in the range 600-1000 tpd capacity, largely based on steam-reforming of either natural gas or naphtha. Centrifugal compressors with steam-driven turbines and for the most part utilized "low pressure" synthesis loops operating at 2200 psia have been generally provided. The advantage of steam-driven centrifugal compressors, when applied to large-capacity ammonia plants is universally recognized but the selection of low pressure for

ammonia synthesis is not so obvious nor is the advantage so universally recognized.

The ammonia synthesis reaction equilibrium and kinetics are favoured with increasing pressure. Condensation of liquid ammonia from the reactor effluent stream at higher temperature also accompanies high pressure operation. The change from high to low pressure synthesis appears to be contrary to chemical engineering principles. With the advent of 1500-2000 tpd plants, consideration is being given to the proper selection of synthesis pressure, such as power for synthesis gas, recycle gas, refrigeration compression, shaft horsepower, efficiency and relative speed for compressor and the usual considerations involving reaction kinetics, conversion efficiency and case of product consideration.

In an article [*Nitrogen*, No. 58, (1969), 25], O. J. Quartulli of M. W. Kellogg Co. has discussed some of the factors with particular emphasis on the horsepower requirements for centrifugal compressors in the fresh make-up synthesis gas, recycle and refrigerant services for synthesis loops operating in the range 2200-4750 psia.

In a typical loop design for a large ammonia plant using the technique of single product condensation, ammonia is withdrawn at a single location at low temperature. After separation of liquid product, vapour is recycled to the ammonia converter, a quench-type vessel having three or four beds of catalyst. For certain situations, two or more converters may be used. Following conversion to ammonia, the effluent from the converter flows after heat removal to the recycle compressor for combination with make-up synthesis gas and recycle compressor may involve use of two or more cases of compression. The refrigeration system usually is provided with several levels of chilling stages depending on the utility cost structure and plant lay-out. For reducing horsepower for the offsite atmospheric storage facilities, product is delivered to the battery limit at about 28°F via run-down through the plant refrigeration system. Ammonia vapours from the storage facilities may be returned to the suction side of the refrigerant compressor. For this loop design, compression of make-up and recycle gases is accomplished in a compressor case having 3 nozzles (two inlet and a single outlet). Because the make-up gas and recycle mixture is chilled after compression, there is no chance of contaminating converter feed due to possible compressor seal oil

leakage, since all contaminants present in the stream are carried with ammonia product. Furthermore, the design of the 3 nozzles compressor case permits an increase in the discharge pressure for a given capacity. By including the recycle wheel in the last stage of the compressor, there is an increase in the volumetric flow of gas and thus the discharge pressure of the machine can be raised.

In the second design the process is the same except that the converter effluent is cooled for product recovery before recycle compression. The converter effluent joins make-up gas at a slightly lower pressure after which the mixture is chilled for products recovery. Disengaged portion then flows to the recycle portion of the compressor from which it is fed to the converter. The synthesis gas compressor has 2 nozzles for make-up gas and 2 for the recycle service.

In the third design operating at 4000 psia the sequence is for a two-stage product condensation system. It consists of chilling converter effluent to an intermediate level for condensation of the bulk of the ammonia contained in the effluent. Condensed ammonia is recovered in a primary separator whilst disengaged gas from this separation step flows to the recycle compressor, where it is combined with make-up gas and further compressed. The combined gas is then water-cooled and chilled for recovery of the remaining product in a secondary separator. The two product streams are merged and delivered to a flash drum to remove dissolved gases.

There are two conclusions that can be drawn in a comparison of low and high-pressure synthesis in the large plant size: (1) There are no appreciable differences in horse-power and fuel consumption when considering a wide range of loop pressures, provided major parameters are maintained constant such as catalyst ageing, product delivery conditions and available pressure of the make-up synthesis gas. On the basis of horse-power alone, the low pressure loop is favoured but that the gap between 2200 and 4750 psia loop operation is small even considering a wide range of process design (2) High loop pressure requires an additional centrifugal compressor case with its attendant high cost and possible higher risk element. If an increase in pressure introduces the need for more moving parts or for heavier, more complex pressure vessels, while yielding no significant operating cost savings then it would be pointless to modify the process design in the direc-

tion of relatively high loop pressure. Raising loop pressure in the interest of reducing recycle and refrigeration bhp is the wrong process route to pursue from a process design standpoint. An increase in synthesis pressure basically shifts the compression service from the refrigerant to the make-up gas compressor. The shift involves a decrease in horse-power for the refrigeration compressor—a low-cost, high efficiency machine of conventional design and an increase in horse power for the h.p. synthesis gas compressor—a high-cost relatively low efficiency machine of special design.

The upshot of the above analysis is that for a 1500 tpd plant there is no economic justification in designing for relatively high synthesis pressure. The appropriate design at this capacity would seem to be one in which the two-case concept employed in most of the 600 and 1000 tpd ammonia plants is maintained for the make-up gas and recycle compressor. Experience reveals that process, mechanical and operational risks associated with this design approach are minimal. A loop pressure in the range 3000-3200 psia meets these requirements although somewhat lower and higher pressure levels could be justified depending on vendor selection, machine design and cost.

[Nitrogen, No. 58, (1969), 21]

Calcination of Phosphate Rock Using the Dorr-Oliver Fluo-Solids System

The suitability of fluidized bed furnaces for the purpose of phosphate rock calcination for its upgradation and commercialization has been described by Dorr-Oliver. The system has been proved advantageous in a number of large-scale phosphate beneficiation ventures in U.S.A. Calcination is often the most efficient way of removing

organic materials which may interfere during processing of the rock to phosphoric acid. Calcination improves rock grades, produces a uniform feed for phosphoric acid manufacture and simultaneously removes moisture and excess carbon dioxide. The advantages and other characteristics of calcination for a typical sample of rock phosphate are given in the table at the bottom of this page based on pilot plant studies.

From the standpoint of improving rock quality, the temperature of calcination is an important factor. For a similar rock to that from which the above data was obtained, it was shown that calcination at 705°C, instead of 815°C, gave a substantially poorer quality product:

Calcination temperature	705°C	815°C
P ₂ O ₅ recovery	93%	95%
Filterability	poor	good
Filter cloth life	poor	6 months

To put the overall advantage of calcination on a cost basis, the estimated savings which can be made in phosphoric acid production have been summarized for a plant using calcined 66 per cent TPL material instead of uncalcined 70 per cent TPL rock:

Cost Advantage of Calcined Rock	Saving, \$/short ton P ₂ O ₅
Defoamer	1.00
Powder	0.14
Improved recovery, 2%	0.44
Reduction in depreciation	0.40
Reduction in labour, supervision and maintenance	1.50
Reduced clarification and desludging costs	0.70
Sub Total	4.18
Credit (for using 66% TPL rock instead of 70% TPL)	2.00
Total saving	\$ 6.18

	Uncalcined	Calcined at 815°C
Rock data		
Water-insoluble P ₂ O ₅	3.3%	2.3%
Citrate-soluble P ₂ O ₅	2.8%	2.2%
Citrate-insoluble P ₂ O ₅	0.5%	0.1%
Acid plant data		
Chemical efficiency	95.8%	97.3%
Filtration rate, s. ton/ft ² day	2.0	3.2
Defoamer (Unitol DSR), lb/s. ton rock	6	zero
Acid colour	dark, turbid	green, clear
Sludging after 1 year	10% vol.	slight

In comparison with other techniques, the particular advantage of the Fluo-Solid system for calcination is the very low maintenance incurrence resulting from the absence of moving parts in the calciner, the necessary agitation being provided by a flow of air.

The calciner itself consists of three distinct compartments, each serving a separate function. In the topmost compartment, into which the process feed is introduced, the feed is preheated by contact with exhaust gases coming, via the hot cyclone, from the calcination compartment immediately below. Beneath the calcination compartment is the cooling compartment, which serves to cool the calcined product by simultaneously pre-heating fluidizing air that subsequently passes upwards into the calcination compartment.

Using a feed containing 12 per cent moisture, the temperature of the exhaust gases from the calcination compartment is reduced in the preheat compartment to 120°C, with simultaneous preheat of the feed material to the same temperature. If substantially less than 12 per cent moisture is contained in the feed, a water spray is used in the preheat compartment to prevent the temperature of the exhaust gases from rising above this limit. The cooled gases pass to the cold cyclone, where most of the entrained particles are removed, and then to the scrubber, whilst the preheated feed is fed at a controlled rate into the calcining compartment, through an external transfer line.

In the calcining compartment, air preheated to 480°C is used both to fluidize the bed of material and to supply the necessary oxygen requirement to maintain the calcination temperature. Depending on the source of the rock, part of the heating requirement for the process is provided by hydrocarbons and other combustible materials contained in the raw phosphate, the remainder of this heating requirement being furnished by the injection of fuel oil into the fluidized bed of calcining material. Exhaust gases from the calcination compartment pass, via the hot cyclone which removes entrained particles of calcined product (–100 mesh), into the preheat section above, whilst the coarser calcined particles (+100 mesh), pass through internal transfer lines into the cooling compartment below.

These coarser calcined particles are used in the cooling compartment to preheat the process air to around 480°C, and after this, the partially cooled calcined product,

together with the separated fines from the hot cyclone, is cooled further to 120°C in the fluidized-bed cooler. This after-cooler incorporates the use of a direct water spray to cool the product, by utilizing the heat of vaporization of water to absorb the sensible heat from the calcine.

The problems arising in the Fluo-Solids calcining system such as the tendency of the rock to be slightly tacky at the calcination temperature and occurrence of scaling, particularly in the ducting of the hot cyclone can be overcome simply by giving exact attention to show procedure in cases where the bed of material has been defluidized and providing for the addition of quench air when there is scaling in the hot cyclone ducting. The quench air reduces the temperature of the hot gases to 595°C a temperature at which the fine rock particles are no longer tacky.

A breakdown of the cost of operating a calciner producing 3,000 stpd of calcined phosphate in two 1,500 stpd using the Fluo-Solids system has been prepared by Dorr-Oliver and the table below shows the summary.

By far the most important fraction in the above table is the cost of fuel.

The cost of calcination per short ton of P_2O_5 produced in a phosphoric acid plant becomes approximately \$2.10 on the basis of calcination cost of 62.4 C per short ton of rock. If this cost is subtracted from the estimated saving of \$6.19 associated with the use of calcined rock in phosphoric acid production a net cost saving of \$4.08 per short ton P_2O_5 is indicated.

[*Sulphur*, No. 41, (1969), 16]

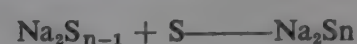
	Cost of Calcined Product (cents/short ton)
<i>Utilities + Labour</i>	
Fuel 500,000 Btu @ 49 C/m.m.Btu.	20.0
Power 12 kWh @ 1C/kWh	12.0
Labour 0.012 man hrs @ \$3.75 per man hr.	4.5
<i>Fixed Costs</i> (capital costs \$ 2.1 million)	
Maintenance @ 2%	4.2
Interest	7.5
Depreciation 15 yr straight line	14.2
Total cost	62.4

Removal of Hydrogen Cyanide from Coke Oven Gas Using Sodium Polysulphide

Soviet Union developed a process to remove hydrogen cyanide from coke oven gas in which hydrogen cyanide is converted into sodium thiocyanate by reaction with sodium polysulphide produced *in situ* by reaction of sodium hydroxide and powdered sulphur. By this technique, the hydrogen cyanide reacts firstly with the sodium ion to form sodium cyanide and then this reacts with the sodium polysulphide as follows:



The lower sulphide, thus produced, is regenerated into the original polysulphide for recirculation by reaction with excess elemental sulphur.



An important feature of this method is that, as the solution circulates, the concentration of sodium thiocyanate increases, thus reducing the solubility of contaminating compounds, such as $Na_2S_2O_3$ and sodium sulphate which are formed in side reactions, so that the level of these impurities is kept relatively low. Crude sodium thiocyanate produced in this way can be purified by solvent extraction or by chemical means.

Interest in this process has been renewed in Czechoslovakia where, after encouraging pilot-plant work, NHKG Steelworks have put a larger plant into operation at Ostrava.

Hydrogen Cyanide Removal: Coke oven gas at 30°C is fed into the bottom of a tall

corresponding nitriles in a single step with high yields (50-60 per cent) in presence of selective catalysts in a flow system in the range 380-410°C the contact time varying from 0.4 to 2 sec. They have also studied ammoxidation of picolines, lutidines, collidines and quinolines, which provides a direct route for their conversion to corresponding cyanoderivates.

Session 5: In this session, the first paper⁴⁷, by J. F. Cudmore of Australian Coal Industry Research Laboratories Ltd., describes the account of work done on the extraction of a number of Australian coals of varying rank using authracene oil and hydrogen under pressure. By this process, it is possible to separate the mineral matter from coal and produce an 'ash-less' extract having a number of possible uses. Finely pulverized coal (— 200 B.S.S. mesh) was mixed with authracene oil and the mixture is placed in a pressure reactor with temperature raised to 400°C slowly. At the end of the reaction the gases are vented and the product is filtered and extracted or distilled under vacuum. This ashless extract, named as coalex, can be carbonized to form a pure carbon which has potential use in making electrodes for the reduction of alumina or it may be hydrogenated to form a synthetic crude which may be converted to gasoline by conventional refining techniques.

J. Roy *et al*⁴⁸ (CFRI) have presented a perspective review of the present status of different mechanisms of solvent extraction of coal vis-a-vis structural implications. The various theories so far advanced for unravelling the mechanism of solvent extraction have been discussed. Based on the concepts of ether, thio-ether and methylene bridge, etc. linkages between the units of coal structure, the authors have discussed the applicability of current theories of heterolytic and homolytic cleavage of structural links, releasing small units easily dispersible in solvents. The recent findings of Heinz Sternberg *et al* on the remarkably high solubility of a high rank coal, on treatment with lithium in hexamethyl phosphoramide or tetrahydrofuran containing naphthalene not only highlights the type of linkage between the units of coal structure but may also elucidate the mechanistic aspects of coal solvation. A fuller knowledge may ultimately lead to the development of a simpler route to the complete dissolution of coal on some suitable solvent.

Y. C. Fu, B. D. Blaustein and A. G. Sharkey⁴⁹ (U.S. Bureau of Mines) have studied that in a microwave discharge in active nitrogen, high volatile coal produces

gaseous products, viz. hydrocyanic acid, acetylene, small amounts of C₂N₂, low molecular weight hydrocarbon gases, carbon and hydrogen oxides; this is analogous to high temperature pyrolysis or discharge pyrolysis either in presence or absence of argon. The reaction occurs in 2 stages: interaction of active nitrogen with coal molecule to cause rapid volatilization of gaseous products and slow gasification of residual char by active nitrogen. Various factors influencing product type, yield and distribution have been examined. Under conditions where gaseous products could be quickly quenched or removed, more than 42 per cent of carbon in coal could be converted to hydrocyanic acid and acetylene, which constitute 90 per cent of the total gaseous products.

G. J. Lawson and R. Haque⁵⁰ (Univ. of Birmingham, U.K.) have subjected one medium rank British coal having 48.91 per cent carbon to low pressure carbonization (600°C) in the presence of various transition metals and their oxides (e.g. 5 per cent of chromium, chromium oxide, cobalt, cobalt oxide, manganese, nickel, etc). The results of the present study confirm those obtained earlier, viz. the proportions of simpler tar acids such as phenols in the tar increased. It was concluded that all the additives reacted with the tar-forming initial decomposition products at the moment of their formation during carbonization. The individual tar acids were analysed by gas chromatography. The yield measurements were supplemented by a thermogravimetric study of the various coal additive mixtures. The changes brought about by the additives in thermogravimetric behaviours were interpreted as shortening the range of temperature over which the thermal decomposition could be considered a first order reaction by increasing the initial temperature of the range.

J. F. Cudmore (Australia) in his second paper⁵¹ has described pilot scale production of coal fertilizers, popularly known as nitrogen-enriched coal (NEC), from a number of Australian coals of various ranks (carbon 69-85 per cent) by simultaneous oxidation and ammoniation in a fluid-bed reactor. The technical feasibility of increasing the nitrogen content of a range of coals by reaction with air and nitrogen has been demonstrated. The investigations included coals of different ranks, and evidence is there that the degree of nitrogen-enrichment increases with decreasing coal rank. The results of evolution of such fertilizers by both laboratory incubation studies and agricultural pot trials have also been pre-

⁴⁷ Dissolution of Coal in Authracene Oil.

⁴⁸ Solvent Extraction of Coals—A Perspective.

⁴⁹ Reaction of Coal with Nitrogen in a Microwave Discharge.

⁵⁰ Studies in the Carbonization of Coal in the Presence of Various Additives.

⁵¹ Nitrogen Enrichment of Some Australian Coals.

sented, which indicate that NEC releases its nitrogen very slowly and that there is need to obtain more balanced release rates. The author maintains that NEC possesses fertilizing potential although it cannot compete with sulphate of ammonia as a fast release fertilizer. He considers that more balanced release rates would be obtained by blending NEC with a conventional fertilizer, like urea.

S. K. Mitra and M. M. Roy⁵² (GSI) from preliminary ammoniation experiments on coal in absence of air or oxygen have shown that the percentage of nitrogen increases with increase in ammoniation time and temperature. By this method a little above 1 per cent nitrogen could be fixed. The changes in proximate and elementary analyses as well as structural analysis have been assumed by chemical and physical methods including i.r. studies, and the changes appear to be due to pyrolysis. But under the conditions of ammoniation, nitrogen is introduced in the form of amide, nitrile and amino groups, the formation of which has been discussed.

The authors have found that in the case of normal matured coal, ammoniation increases and the disordered part of the coal structure decreases with increase in ammoniation time and temperature. I.R. spectral data also support the fact that ring closure ensues at higher temperature and time of ammoniation. This study however merits further attention in view of its obvious importance in understanding the mechanism of nitrogen fixation and finally the state of nitrogen in NEC.

The next paper⁵³, by L. V. Ramchandran, D. S. Chatterjee, P. N. Mukherjee and A. Lahiri (CFRI), deals with the state of nitrogen in NEC, which is necessary for a proper appreciation of the character of nitrogen to elucidate the slow release nature of such fertilizers. For a typical sample of NEC, containing about 18 per cent nitrogen, hardly 1/3rd is available and this is considered to be maximum proportion that is likely to be available to plant under field conditions. Following this, the authors have studied the distribution of nitrogen in the products of oxidation of coal fertilizer and found that 60-100 per cent of the nitrogen is released in the form of ammoniacal and nitrate nitrogen of which the major portion (60-80 per cent) is ammonium. The distribution as obtained by alkaline-permanganate oxidation appears to depend on the original level of nitrogen fixation in the NEC. Higher the percentage of nitrogen fixed, higher is the proportion of ammoniacal nitrogen formed on alkaline

permanganate oxidation and consequently lower the nitrate nitrogen. The authors therefore suggest the possibility of structures like *p*-aminobenzoic acid, diethanolamine, diphenylamine carbazole, etc. in NEC.

The last but one paper on coal fertilizers⁵⁴, by N. B. Paul and G. Singh (CFRI), deals with pot experiments conducted under green house conditions on maize crop showing the effect of humic acids prepared from lignite and farmyard manure. Humic acids added at 0.01 and 0.05 per cent to the soil gave significantly higher yield of crop, uptake of nitrogen by crop and its nitrogen content over control. At the higher dose (0.05) the crop yield in the case of lignite humic acid was higher (65 per cent) than in the case of FYM acid (58 per cent). The reasons for this stimulating effect are: (1) humic acids stimulate nitrogen fixation by *Azotobacter*, (2) the latter synthesize certain growth-promoting substances, (3) the increase in total bacterial count in soil is directly related to improvement in soil fertility, (4) humic acids influence the metabolism of plants. In a tropical country like India, where soils are generally deficient in humus, large-scale application of humic acids may go a long way to solve soil fertility.

The last paper on coal fertilizers was by L. V. Ramchandran, T. Saran, P. N. Mukherjee and A. Lahiri⁵⁵ (CFRI). The authors presented the results of slow and shock pyrolysis of a sample of NEC containing 17.73 per cent nitrogen primarily with the idea of establishing optimum conditions for the maximum production of hydrocyanic acid—its yield on slow pyrolysis (5°C/min.) at 900-1200°C remains virtually constant (60 lb/ton), a conversion of 8 per cent of nitrogen, but on shock-heating pyrolysis at that temperature range the yield increases with increase in temperature (266 lb HCN/ton at 1200°C). The latter corresponds to a conversion of about 36 per cent of nitrogen to hydrocyanic acid. The authors have discussed various probable mechanisms of the latter's formation from a comparative study of the behaviour of urea under identical conditions of pyrolysis. They finally concluded that in view of low conversion and loss of about 2/3rd nitrogen as ammonia and free nitrogen, the production of hydrocyanic acid from NEC would not be economically feasible.

B. K. Mazumdar *et al*⁵⁶ (CFRI) have studied control-

⁵⁴ Crop Response with Humic Acids from Coal.

⁵⁵ Formation of Hydrocyanic Acid by the Pyrolysis of Nitrogen-enriched Coal.

⁵⁶ Aromatic Polycarboxylic Acids by Nitric Acid Oxidation of Coal & Their Potentialities by B. K. Mazumdar, A. Banerjee, J. M. Sanyal, S. Ganguly, A. K. Chatterjee, P. K. Sanyal and A. Lahiri.

⁵² Studies on Ammoniation of Coal Related Products—I.

⁵³ A Study of the State of Nitrogen in the Nitrogen-enriched coal.

led oxidation for direct conversion of the organic complex of coal to simpler chemicals, essentially aromatics. It had long been the dream of coal chemists to prepare aromatic chemicals by simple oxidation to aromatic polycarboxylic acids and ultimately to benzene carboxylic acids. So far nitric acid had been the oxidizing agent with no promising results. However, the authors have carried out a systematic study with nitric acid and have shown that successive action of conc. nitric acid completely converts low rank coals, including lignite, into water-soluble polycarboxylic acids which are immune to further degradation by fuming or conc. nitric acid. Preliminary characterization of the gross oxidation product by equivalent weight, molecular weight and elementary analysis as well as a study of its response to phthalein reaction appear to indicate that under the mode of treatment more of simpler benzene carboxylic acids, like di- and tricarboxylic acids, are perhaps formed than have hitherto been recovered and identified. Attempts have been made to prepare phthalein derivatives, e.g. phenol-phthalein, fluorescein and eosin. The yield of such nitrophthalein derivatives has been found to be significantly high, varying from 100 to 250 per cent (of the polyacids depending upon the type of products derived. The elementary composition and behaviour of such derivatives compare favourably with those of the corresponding standard substances prepared from standard nitro-phthalic anhydride.

The significance of these tentative findings and the potentialities of these acids as intermediates for production of intermediate products and chemicals directly from coal has been discussed.

A proper appreciation of the aromatic portion in the coal structure is the key to develop a new utilization of coal. From the results obtained in some of the typical authentic hydrocarbons, M. Itoh, S. Yokoyama, M. Makabe and G. Takeya⁵⁷ of the University of Hokkaido (Japan) have found that the rate of the deuteration of aromatic hydrogen was much faster than that of aliphatic hydrogen, when the reaction was carried out at the temperature that did not cause disproportion or rearrangement of side chain to occur.

For the selective deuteration of aromatic hydrogen, the optimum range of reaction temperature to be adequate was from ordinary temperature upto 65°C. A higher temperature caused disproportionation to occur in the case of cumene. The reagent should be ten times or more of the equivalent. The rate of reaction was

usually very fast, but at least 2 hr. of reaction time seemed to be necessary to complete the reaction.

The authors have applied deuteration method for the pyridine extract of a typical bituminous coal. The pyridine extract had a little more volatile matter and polar portion than the raw material but the difference of average structural units between them was very little.

N. V. R. Appa Rao, G. S. Murty, H. S. Rao and A. Lahiri (CFRI)⁵⁸ have suggested a conceptual structure of "Stringed Rafts in a Eddy" for Coals of Assam. Their study is based on high resolution proton magnetic resonance spectra of gamma-picoline extract of Assam coal and other chemical data.

Assam coal is rich in sulphur (usually 3-8 per cent), of which over 90 per cent is in organic form. The reserves of these are over 3800 million tons. M. S. Iyengar and J. L. Ghose⁵⁹ (RRL, Jorhat, Assam) have described various methods for the recovery of sulphur. The following two approaches have been investigated in their laboratory: (1) by controlled combustion of coal in a furnace at 800°C aiming at maximum conversion of sulphur to sulphur dioxide followed by its absorption in caustic soda or ammonium carbonate solution or in a bed of limestone at 700°C; (2) desulphurization technique under partial combustion conditions with limited supply of oxygen or carbonization with or without catalysts and/or additives like alumina, zinc sulphide, etc.

In the first process under optimum conditions 80-90 percent sulphur may be recovered in the form of sodium sulphite, ammonium sulphite or ammonium sulphate and calcium sulphate depending upon the absorption media used. In the second approach, which is more economic and practical, 5 per cent alumina as additives is added. Combustion under limited supply of oxygen at 600-750°C reduces sulphur content of coke by about 60 per cent. The effect is due to catalytic selective oxidation of organic sulphur in preference to carbon. The author concludes that this additive carbonization can provide simple methods of desulphurization and subsequent recovery of sulphur from Assam coals.

The peroxidation method⁶⁰ by A. J. Nalwalk and R. A. Friedel (US Bureau of Mines) for selective oxidation of organic matter without affecting the mineral matter is simple and inexpensive. By this method removal of nearly all organic material from coals as

⁵⁷ Deuteration of Aromatic Hydrocarbon and Coal Extracts for the Study of the Average Structural Units of Coal.

⁵⁸ Conceptual Structure of Assam Coal.

⁵⁹ On the Recovery of Sulphur from High Sulphur Assam coals.

⁶⁰ Concentration of Minerals in Coal by Peroxidation of the Organic Matter.

carbon dioxide and water can be accomplished with 35 per cent hydrogen peroxide at low temperatures (below 100°C). It will (1) remove most of the organic material and concentrate the minerals (2) not destroy or alter most of thermo-organic minerals, (3) allow mineral identification by x-ray or i.r. and (4) permit determination of the percentages of some minerals. This method is slower than the plasma technique but a combination of the two should be useful.

K. Littlewood (Univ. of Sheffield, U.K.) presents⁶¹ recent developments on the production of acetylene as obtained by argon or argon/hydrogen plasma jet reactions. If pulverized coal is heated rapidly to about 1250°C, the emitted volatile matter is cracked to get low molecular weight hydrocarbons consisting mainly of acetylene. From the consideration of free energy of formation of hydrocarbons, which consists mainly of acetylene, around 3500°K conversion to acetylene should be maximum, but this may be somewhat offset by a number of undesirable side-reactions, e.g. formation of higher acetylenes, benzene, etc. or the decomposition of acetylene.

Two high temperature devices have been investigated viz., an arc furnace and an argon plasma jet, the former suitable for static conditions, and the latter to flow conditions. Optimum conditions for the production of acetylene using an arc-image furnace were found to be a heat flux value of 42 cal. cm⁻² sec⁻¹, an irradiation time of 2 min. a coal particle size of—300 mesh and a coal sample of 0.1 g. The weight of carbon converted to acetylene increases with decreasing C/H ratio of the coal. A C/H ratio of 16 or less appears to be critical not only for the production of acetylene but also for other lower hydrocarbons.

In the flow system such as an argon plasma jet, the greatest difficulty is the efficiency of mixing of the coal/carriers gas and hot plasma streams. Two mixing procedures have been investigated.

In the last paper, the author, P. K. Daradhiyar⁶² of H. D. Jain College, Arrah, reports isolation of a species of *Asperigillus* in the fungal population of a coal-debris soil and this has been identified to be *Asperigillus Sparsus Raper* and *Thom*. The fungus was cultured in Czapek's Agar liquid medium and the fungal colonies were dull greyish becoming darker on standing without an odour. It grows best at 250°C and pH 6.5 The fungus was grown in Czapek's Agar medium containing auto-

claved coal-debris soil in different proportions. So far 6 species of *Asperigillus* have been isolated from the soil of Bihar but none from coal-debris had been reported. It is anticipated that this fungus will open a new chapter of coal research in the future.

Summing up: While summing up the proceedings of the symposium, Dr. A. Lahiri, Director Central Fuel Research Institute, dealt with paper by paper sessionwise. He elaborated the work being carried out at CFRI on all aspects of coal utilization, including solvent extraction of coal, preparation of catalysts and coal fertilizers, etc and particularly on using coal as a source of secondary energy. The symposium made the following recommendations for active consideration in the immediate future: (1) CFRI prepared a preliminary but interesting account of the status of the art and feasibility study of oil from coal. The problem centres round development of effective catalysts for liquefaction of coal. Depending on the resources and economy—local, regional or national—the total concept of project to coal conversion will have to be conceived and plans made. (2) References were made to the work in Japan, Germany, USA, Czechoslovakia and India regarding fundamental concepts for basic understanding of the reaction mechanisms involved in the conversion of coal to oil and chemicals by hydrogenation, oxidation, halogenation, etc. Further studies on these aspects were considered necessary. (3) Production of chemicals by the versatile technique of Fischer-Tropsch synthesis has great potentialities which must not be overlooked. Recovery and utilization of tar oils, benzole, naphthalene and anthracene deserve special attention and CFRI activities in this field were received with interest. The solvent extraction route for the enrichment and recovery from coal tar oils, the possibilities of the ammoxidation route for obtaining pharmaceutical intermediates, from tar basis nitrogen enriched products for use as fertilizers, etc, should be pursued in view of their wide industrial application. Microbiological approach for making the organic fertilizer, rich in nitrogen in the soil should be pursued. Work in this direction by Russian group of workers should serve as a guideline. (4) Canadian and US scientists have already achieved a lot on the decarboxylation of coal acids, which may be of a potential breakthrough in this field. The activities of the Planning and Development Division of the Fertilizer Corporation of India for developing active catalysts for gas reforming, purification, etc. deserve special mention.

Petroleum Feedstocks for Ammonia Manufacture

The main commercial sources of hydrogen are water,

⁶¹ The Direct Production of Acetylene from Coal.

⁶² Isolation of a Species of *Aspergillus* from Coal-Debris Soil from Chaibasa (Singbhum)—A New Record for India.

hydrocarbons, coal or lignite. There are two types of processes for production of hydrogen, viz. direct and by-product recovery. While the direct processes are electrolysis of water, and use of steam to convert hydrocarbons, coal, iron oxide, etc. into hydrogen, the by-product processes are mainly coal carbonization, catalytic reforming and olefine manufacture.

The role of the hydrocarbon in hydrogen production is not only to make it hydrogen-free but to provide a source of energy for the reaction. Per mole of water decomposed and per unit hydrogen produced, the energy required for electrolysis of water is the highest. In actual practice, due to heat losses, the energy requirements of hydrocarbon gasification processes increase.

The important processes for gasification of hydrocarbons can be classified as follows: (1) Thermal, cyclic-carburetted water gas, Jones, Hall & Semet-Solvay; (2) catalytic, cyclic-ONIA - GEGI, Segas, Stein et Roubaix, Gaz de France; (3) Thermal, continuous Shell, Texaco, Montecatini; (4) Catalytic, continuous—CCC, ICI, Topsoe—SBA, Distrigas. The raw materials originating from petroleum sources that can be used for synthesis gas production are: natural gas ($H/C = 3.75$); refinery gases (2.3-2.9), light distillates (2.2), heavy oils (1.6) and residues (1.6).

Under the auspices of the Fertilizer Association of India, Dr. M. G. Krishna, Director, Indian Institute of Petroleum (CSIR), delivered a lecture at New Delhi on July 28, 1969 with Sri N. N. Kashyap, Chairman, Indian Oil Corporation Ltd., presiding. Dr. Krishna stated that the cyclic processes—thermal and catalytic—are primarily meant for town gas manufacture; however, they can be adapted to produce synthesis gas for ammonia manufacture. The thermal cyclic processes operate at high temperature (800-1000°C), low residence and nearly atmospheric pressure so as to favour cracking reactions and minimize polymerization and coke-forming reactions. These processes have the disadvantage of high carbon deposition and therefore longer or frequent blow cycles, when heavy hydrocarbons are used.

The catalytic cyclic processes use mostly nickel catalyst (ONIA-GEGI, Stein et Roubaix, Gaz de France) and also lime and magnesia catalysts (Segas). In principle, the oil is burnt in a preliminary chamber and the combustion products heat the catalyst bed and the excess air burns off the carbon and sulphur compounds deposited on the catalyst. This is followed by the 'make' cycle in which oil vapours are gasified on the catalyst bed. The carbon and tar formation are minimized in the catalytic processes, which are particularly suitable for gasification of light distillates. Attempts have been made to

operate these plants at higher pressures, as they are generally operated at atmospheric pressure and about 900°C.

The thermal continuous processes—the most important being the Shell and Texaco—operated on the principle that part of the hydrocarbon is burnt providing the heat to raise the temperature of the reactants (1300-1500°C) to the desired level. Pressures are kept at 30-35 atm. and the minimum quantity of oxygen necessary for complete hydrocarbon conversion is 0.5 K mole per K atom of carbon. For heavier hydrocarbons, containing olefines and aromatics, the adiabatic reaction temperatures are much higher than practical levels. Therefore, usually steam is admitted with the reactant streams to control temperatures. The steam also reacts endothermically with hydrocarbons and simultaneously controls the temperature, its additional role is to suppress carbon formation by reacting with olefinic intermediates formed by thermal cracking of hydrocarbons at the high temperatures in the reactor, which would otherwise polymerize and condense to form carbon. It is thus essential to ensure thorough mixing and distribution of steam in partial oxidation processes. A major advantage of these processes is their ability of use a variety of feedstocks without major changes in the plant. In Europe these processes are widely used. In a BASF plant (W. Germany), the Texaco process has been operated upto 82 atm.; carbon can be recycled. The Shell process is also undergoing improvements. The credit given to carbon recovery is important in the economics of the partial oxidation processes.

In the catalytic continuous processes, the main reaction is strongly endothermic, between hydrocarbon and steam, producing carbon monoxide and hydrogen; the mildly exothermic shift reaction between carbon monoxide and steam also occurs. The steam-reforming reaction is favoured by high temperature, lower pressure and higher hydrocarbon ratio. Among the processes using external heat, ICI and Chemico are well-known; among the internally-heated steam-reforming processes, the Topsoe, SBA and the Distrigas processes are important.

The thermal cyclic and continuous processes have a wide flexibility of feedstock selection and can use heavy fuels having Conradson carbon going upto 16-17 per cent. The catalytic processes, most of which use nickel catalysts, are however sensitive to feedstock characteristics, particularly the contents of sulphur, olefines and aromatics. It is generally accepted that in the naphtha feed for the ICI process sulphur should be less than 5 ppm, unsaturates other than benzene upto one per cent and benzene and other aromatics less than 12 per cent.

However, R. J. Young of ICI has stated that "there is no limit to sulphur or to its aromatic content, as the special reforming catalyst can treat all gaseous hydrocarbons including C₃ and C₄ containing upto 20 per cent unsaturates.....; and the feedstock is a straight-run naphtha with a final boiling point not more than 200°C". It therefore appears that lighter gaseous olefines can be processed but heavier olefines above C₅ should be strictly limited; no limit has been fixed for naphthene content. From the properties of naphtha from Indian crudes (Table 1), Dr. Krishna recommends that Ankleshwar naphtha can be used as it is, while Nahorkatiya naphtha needs desulphurization (however, in view of R. J. Young's remarks there is no need). As regards suitability of hydrocracked naphthas, the speaker believes that there should not be any objection to their use in the ICI process because of their high proportions of

isoparaffins and naphthenes; the main objection against these would be the price. Most of the hydrocrackers in the world are presently operating on lighter or heavier distillates and straight run or cracked or recycled stock with a view to produce a variety of products such as LPG, high octane gasoline stocks, jet fuels, diesels and fuel oils with low sulphur content. Today only one hydrocracker is operating (in Kuwait) on heavy residues using H-oil process and the performance is reported to be satisfactory. The hydrogen consumption and the processing cost depend upon the products and feedstocks. Generally, the heavier the feedstocks and the lighter the products, the more will be the hydrogen consumption and cost. Therefore, the justification for use of hydrocracked naphtha rests entirely on its price. The residual fuel oils (Table 2) from Indian crudes are quite satisfactory for use in the partial oxidation process.

TABLE 1—CHARACTERISTICS OF NAPHTHAS FROM DIFFERENT INDIAN CRUDES

Property	Crude	Ankleshwar (46.8° API)		Nahorkatiya (34° API)	
		C ₅ -175	C ₅ -200	C ₅ -175	C ₅ -200°C
1. Gravity 15/15°C		0.735	0.742	0.75	0.771
2. Yield on crude (W.T. per cent)		33.5	39.0	22.8	27.8
3. Sulphur (W.T. per cent)					
a. Total		—	—	0.06	0.06
b. Mercaptans		—	—	—	—
4. C/H Ratio		6.11	6.29	6.55	6.70
	P	57	60	38	34
5. Pona (Vol per cent)	N	34	30	37	36
	A	9	10	25	30

TABLE 2—PROPERTIES OF RESIDUAL FUELS FROM INDIAN CRUDES

Property	Residue from	
	Ankleshwar	Nahorkatiya
Density (15°C)	0.8775	1.9927
IBP, °C	268	270
FBP, °C	512	540
Flash point, °C	156	72
Pour point, °C	48	45
Carbon residue, per cent wt.	1.40	5.50
Sulphur, per cent wt.	0.20	0.59
Ash, per cent wt.	0.01	—

Availability: The proved and indicated reserves of natural gas, which is the best raw material for ammonia manufacture, are about 67 billion m³. It is estimated that by 1973 the need of naphtha would be about 1.9 million tonnes by firm projects and 0.9 m. tonnes by the likely projects which is expected to rise to about 1.7 million tonnes by 1975. The rise in total demand for petroleum products is almost wholly accounted for by the demand for naphtha. Unless refining capacity is adequately increased during 1973-75, the shortfall can not be met.

The residual fuels are currently sold under the names LSHS (low sulphur heavy stock) and HHS and their production depends on the market and crude processed. During 1973-75, about 2 million tonnes of these fuels would be produced with the all-India refining capacity at below 27 millions. If extra refining capacity is installed during 1973-75, more of the residuals will be available, which can be satisfactorily used for ammonia production.

The gap would depend upon the policy of providing feedstocks for nitrogenous fertilizer industry. In the opinion of Dr. Krishna the more we diversify the feedstock selection, the more manageable will be the position of availability. Considering the naphtha deficit additional refining has to be planned mainly to make up for the naphtha deficit, over 10 million tonnes of additional crude has to be refined in 1974-75. This would be quite undesirable because the consequential production of other products would be far in excess of demand. It is therefore very desirable to balance the use of various products and make a judicious selection of available modern technology to suit Indian requirements and context, and in this balancing consideration should be given to make the maximum use of natural gas for ammonia manufacture, instead of using it as a fuel gas.

Process Considerations: While the partial oxidation processes have better flexibility on choice of feedstock, their plant and operational costs are generally higher, particularly for oxygen and steam requirements and also for purification of gas. The capital cost of plant for steam-reforming process is estimated to be about 75 per cent of that for partial oxidation process.

The hydrocracked naphtha is estimated to cost about Rs. 220/te starting with a feedstock price of Rs. 110/-, so if residual oil is available at a cheaper rate partial oxidation process would be advantageous. The price of fuel oil ex-refinery depending upon location varies between Rs. 180 and 200/-. This has to be compared with the price of Rs. 200/tonne of hydrocracker naphtha, in estimating the cost of which it was assumed that middle distillate production would be maximized to

meet the local demand, since the demand for high octane motor gasoline in India is very limited. In that case the surplus hydrocracked naphtha would also be available for ammonia manufacture.

Fertilizer Production and Technology

A national seminar on fertilizer production and technology, organized by the Fertilizer Association of India, was held in New Delhi in Dec. 14-16, 1969. Papers connected with development and experience gained in the production of ammonia, urea, phosphoric acid and complex fertilizers were presented.

The design of large single-stream ammonia plants and the general features of steam-reforming and ammonia synthesis were dealt¹ with giving the difficulties in the commissioning and operating new plants by the ICI. Operating features of twelve naphtha reforming plants installed by ICI in U.K. during 1960 were discussed. From experience gained steps have been recommended to overcome the difficulties.

A participant from Shriram Chemical Industries, Kota discussed² the features of a 450 tpd ammonia plant, a single stream unit employing Topsoe steam-naphtha reforming process. Carbon dioxide removal is done by the modified Benfield process. The plant has not faced any major operating problem except some potash migration from the primary reformer catalyst and some damage to the secondary reformer refractory lining. The project has been described as a complete success. The operating experience of an ammonia plant in Gujarat based on ICI's naphtha-steam-reforming process with problems like process design limitations, operating problems with the process, machinery and equipment failures and utility supply failures and the measures adopted to overcome these difficulties have been discussed.

In the case study of preventive maintenance of ammonia plant, Mr. B. Jagga Rao of Coromandel Fertilizers Ltd. discussed³ the objective of a well-planned and properly conducted efficient P.M. Programme to keep the unscheduled downtime to a minimum by having a series of logical routine inspections and adjustments to equipment to find out and repair small items before they become serious. A master lubrication schedule is prepared and followed for P.M. lubrication check-ups.

¹ Steam-Reforming of Hydrocarbons in Ammonia Synthesis by G. O. Morgan.

² Case Study of Operation (including breakdowns) of Ammonia Plant by S. K. Subbaroyan.

³ Case Study of Preventive Maintenance of Ammonia Plant.

The programme can be achieved in several different ways, such as (i) minimum production downtime, (ii) less long scale repairs, (iii) fewer breakdowns, (iv) eliminating premature replacement of machinery and equipment, (v) best economical use of maintenance manpower as a result of working on a planned basis rather than on attack basis to repair breakdowns, (vi) improve safety and working conditions, (vii) reduced cost of repairs, (viii) screening out equipment with excessive maintenance costs and pin-pointing the need for corrective maintenance or better operation or replacement of obsolete equipment and (ix) by establishing enough stock of spares and proper tools and jigs and by well explained maintenance procedures.

In a paper by P. C. Sharma⁴, the salient features of production of synthesis gas at FACT by the naphtha-reforming as well as partial oxidation route have been discussed. The duties on various units, such as shift conversion and carbon dioxide removal, etc. in the various streams, are dealt with. The cost of equipment for an ammonia plant based on partial oxidation is expected to be nearly 40 per cent higher than the one using the reforming route. The naphtha consumption per ton of ammonia being almost the same, the partial oxidation based plant requires nearly 75 per cent more electric power (synthesis gas compression by reciprocating compressors). The latest developments in increasing the partial oxidation pressure to nearly 100 atm are likely to make this route quite attractive. The cost of ammonia will also be very competitive with the additional advantage of using a wide range of feedstocks.

In the paper, entitled 'Contribution of Materials Technology in Fertilizer Plants' by C. A. Edeleanu and A. K. Bhattacharyya (ICI), the optimum selection of a material or a product considering the factors, such as cost and construction period, has been discussed. The authors compare the performances of equipments in service and select the best material.

S. P. S. Andrew of ICI (U.K.) discussed⁵ the role of catalysts for the production of ammonia. Modern large-scale ammonia production is critically dependent on the performance of seven catalytic processes which, following in series, comprise the chemical steps in the production of ammonia. These seven heterogeneously catalysed processes, viz. hydrosulphurization, primary and secondary reforming, high and low temperature water gas shift reaction, methanation and finally ammo-

nia synthesis require catalysts in which the virtues of good selectivity, high activity, long life, adequate strength, correct particle shape, and predictable performance are combined with cost to give the ammonia producer the optimum advantage. In his paper each of these properties has been considered in turn and the scientific basis used by the catalyst manufacturer in seeking to obtain them is outlined with particular reference to the demands and duties placed on catalysts for the production of ammonia.

In the paper 'Latest Designs of Ammonia Synthesis Converters' by K. J. Mundo (Uhde), the classical type of converters, viz. the tube cooled and the quench-type, are described briefly. The special features of the Topsoe radial-flow converter, the ICI modification of the quench converter, the OSW-Uhde high grade heat recovery converter and the Czech designed spherical converter are brought out.

Phosphoric Acid

In the paper 'Recent Developments of Phosphoric Acid' Sarbasri B. B. Roy and A. K. Roy of the Planning and Development Division, FCI Ltd., discussed the various techniques of phosphoric acid manufacture stating their merits and demerits. In the wet process various techniques based on dihydrate, hemihydrate and anhydrite and combination of hemihydrate-dihydrate technique and *vice versa* have been stated in brief. Recent developments in the preparation of the acid through hydrochloric acid route by the use of solvent extraction technique, superphosphoric acid production and the furnace process have also been described. In short, considerable improvement has been taking place in the development of high efficiency filter construction. Possible utilization of by-product gypsum under Indian conditions and choice of a suitable process which is likely to produce a good quality gypsum along with other operational and economic advantages have been discussed at length. Utilization of gypsum for cement-sulphuric acid production and the choice of a combined hemihydrate dihydrate technique seems to be the most logical one at the present moment under Indian conditions.

J. L. Thakkar⁶ of Dharamsi Morarji Chemical Co. Bombay, discussed the selection of raw materials in the manufacture of phosphoric acid by the wet process, the usual impurities contained in the rock phosphate and their effect on the process. The alternate sources of

⁴ Case Study of Synthesis Gas Production at Fertilizer & Chemicals (Travancore).

⁵ Catalysts for the Production of Ammonia.

⁶ Selection of Raw Materials for Phosphoric Acid.

carbon decreases with pressure and increased with temperature.

From the conversion data, hydrogen consumption, gas formation, hydrogen enrichment of the liquid products, yields of distillate (200-300°C) and the amount of saturates in the distillate, the authors deduce that at 250 kg./cm². reaction pressure, the most favourable temperature range for hydrogenation is 400 to 420°C to yield a maximum of the desired middle distillates. The loss of carbon as gas may be somewhat higher at temperatures above 400°C, but this is likely to be compensated by increased conversion, increased yield of middle boiling distillates containing higher amounts of saturates and a decrease in residence times.

Herbert R. Appel, Irving Wender and Ronald D. Miller of the U.S. Bureau of Mines have presented¹³ a novel approach to coal hydrogenation. They have demonstrated the feasibility of using a mixture of carbon monoxide and water for hydrogenating coal to yield an oil which could then be converted to more volatile fuels by known techniques. In autoclave experiments at 4500 psig and 380°C, conversion of lignite was nearly 95 per cent, although for bituminous coal conversion did not exceed 75 per cent.

A noteworthy comparison is that when CO+H₂O was used at 380°C, the reaction was complete in 10 min. whereas with hydrogen only 50 per cent conversion took place in this time. The effectiveness of carbon monoxide and water in solubilizing low rank coal may be due to a number of reasons including (i) hydrogenation with activated hydrogen produced by the water gas shift reaction, (ii) the introduction of alkyl groups and (iii) the unique ability of carbon monoxide to cleave certain types of bonds or to inhibit condensation reactions leading to benzene in soluble materials.

A number of pure compounds were also tested for their case of hydrogenation with carbon monoxide and water and with hydrogen. The case for conversion of cellulose and glucose to benzene-soluble products with carbon monoxide and water suggests that the structural units derived from those found in carbohydrates exist in low rank coals, an observation of interest in relation to proposed structures for low rank coals.

In their paper¹⁴, N. P. Morparia and S. Sarkar of IIT, Bombay have studied hydrogenation of neutral oil

fractions of G. P. 200-350°C in a reactor of 350 ml capacity with the objective of producing diesel oil. With a commercial cobalt-molybdenum-alumina catalyst (3 mm. × 3 mm.) under the optimum conditions of 400°C 100 kg./cm² and 0.5 liquid space velocity, the yield of the desired product (200-350°C) was 68.6 per cent. At lower temperatures the degree of hydrogenation was less, while higher temperatures resulted in excessive cracking. Better results were obtained at lower space velocities. The cetane number of the product was 35.5 and the smoke point 13 mm. which satisfy the ISI specification for diesel and kerosene.

(Mrs.) A. Mizra, M. A. Masood, M. M. Mallikarjun and R. Vaidyeswaran of R. R. L. Hyderabad have studied¹⁵ hydrogenation of a neutral oil fraction (200-300°C) of l.t. tar with a view to get diesel and kerosene. Hydrorefining of the raw neutral oil was done with cobalt molybdate on alumina catalyst and for the hydrogenation of the raw and hydrorefined neutral oil tungsten sulphide-nickel sulphide on alumina catalyst was used. Their runs were carried out in a 60 c.c. bench-scale unit as well as in an 1-litre pilot plant in a single as well as two stages using the above two types of commercial catalysts. This study led to the following: (1) using cobalt molybdate on alumina for hydrorefining, about 55 and 40 per cent sulphur and nitrogen respectively could be removed. Although the aromatics content could not be brought down sufficiently, the product conformed to grade II diesel, (2) with tungsten sulphide-nickel sulphide on alumina and at a space velocity of 0.2-0.3 both hydrorefining and saturation could be accomplished and the aromatics could be reduced to less than 20 per cent; (3) in the 2-stage operation, a product with a smoke point 22 mm. could be obtained at a space velocity of 1 for both operation by first hydrorefining with cobalt molybdate and subsequently subjecting the product to hydrogenation in a second stage on a tungsten sulphide-nickel sulphide catalyst; (4) recycling of tail gases helped in maintaining hydrogen sulphide concentrations in the gas which advantageously retains the catalyst in sulphide form; (5) hydrogen consumption has been estimated to be 170 and 150 m³/te respectively for the first and second stages of operation; (6) use of tungsten sulphide-nickel sulphide catalyst in 2 stages was found more effective than in a single stage operation.

A fraction distilled (200-350°C) from low temperature tar obtained in a pilot plant from Raniganj coal was

¹³ Dissimilar Behaviour of Carbon Monoxide Plus Water and of Hydrogen in Hydrogenation.

¹⁴ Studies of L. T. Coal Tar Hydrogenation: Part I—Hydrogenation of Neutral Middle Distillate in a Continuous Bench-Scale Unit.

¹⁵ Possibilities of Producing Middle Distillates from L. T. Tar Fraction.

collected and tar acids and bases were removed from it by the conventional washing treatments. The resultant neutral oil was washed, dried and treated¹⁶ in a continuous vapour phase reactor using molybdenum trisulphide pellets with over 98 per cent pure hydrogen at 375-400°C, 1500 lb/sq. in. pressure and space velocity 0.5-1.0 by B. B. Brahmachari, M. R. Saha, P. B. Choudhury and A. K. Ganguly (CFRI).

The hydrogenated product did not contain any olefinic hydrocarbons and showed an increase in the paraffinic carbon at the expense of the aromatic carbon, the naphthenic carbon content remaining more or less at the same level. It is inferred that the conversion of aromatic to paraffinic carbons has taken place via the formation of naphthenes. The smoke point of the kerosene fraction was below 20 mm. and as such did not conform to ISI specifications. The diesel fraction with diesel index of more than 45 could however be used as high speed diesel.

S. Basu and V. A. Krishnamurthy (CFRI) have synthesized¹⁷ oxygenated chemicals consisting mainly of alcohol by the hydrogenation of carbon monoxide using nitrided iron catalyst in a fluid bed reactor. The catalyst was found to be highly active with a gas conversion rate of 1375 vol/vol of cat/hr. at 320°C and 150 psi. The liquid products contained upto 60 per cent of oxygenated chemicals and the yields of these decreased with increase in temperature and also with decrease in space velocity.

The following are the authors' conclusions: (1) higher yield of lower hydrocarbons (gaseous) have been obtained using nitrided iron catalysts and also as a result of using fluid-bed technique at high temperature, (2) usage ratio is always lower than the feed gas ratio and is strongly dependent on the extent of conversion and feed gas ratios, (3) the nitrided iron catalyst has yielded liquid products containing upto 60 per cent of oxygenated products and the yield of these chemicals decreased with the increase of reaction temperature and also with decrease in space velocities, (4) the catalyst was highly active and could convert about 1373 volumes of synthesis gas ($\text{CO} + \text{H}_2$)/vol cat/hr. at 320°C and 150 psig, and (5) at the end of tests the excessive pressure drop encountered was due to deposition of waxy hydrocarbons on the catalyst particles.

Prof. H. Kolbel and J. Trapper, of the Technical

University, Berlin, have developed¹⁸ a single stage amine synthesis in which steam instead of hydrogen is used on a fixed bed on a fixed reduced iron catalyst in an electrically heated tube of 15 mm. I.D. and 60 cm. length. A mixture of carbon monoxide, steam and ammonia in presence of reduced iron catalyst at 11 atm. and 250°C yields a carbon monoxide conversion of 90-95 per cent, ammonia conversion 70-80 per cent at a flow rate of 350-370° SI/h/1. of cat. The synthesis product consists of primary unbranched monoamines with exclusively terminal NH_2 groups together with saturated and unsaturated predominantly unbranched hydrocarbons (molar ratio amines: hydrocarbons=1:5). In side reactions, formation of alcohols and carboxylic acids can occur.

Secondary amines are present in traces. The yield of primary, unbranched amines was 10-15 g/Sm³ of carbon monoxide converted to 4.2 g./g. ammonia converted. The homologues methyl amine upto dodecylamine were identified. Increasing potassium carbonate content of the catalyst results in increased amines formation. The reaction is of the 0.6 order with respect to ammonia.

Controlled air oxidation of coal yields a mixture of aromatic acids ranging all the way from phthalic acid to mellitic acids in about 50 per cent yield. Selective decarboxylation of these benzene polycarboxylic acids to a simple mixture of isophthalic and terephthalic acids has been made possible¹⁹ by the use of dicobalt octacarbonyl and some of its derivatives.

In the presence of carbon monoxide and hydrogen, dicobalt octacarbonyl catalyses the selective partial decarboxylation of phthalic acid or anhydride and substituted phthalic acids and anhydrides to yield the corresponding benzoic acids. In the case of pyromellitic acid, the dicobalt octacarbonyl is consumed in the decarboxylation, becoming a reactant instead of a catalyst. However, by using derivatives of dicobalt octacarbonyl in which two carbonyl groups are replaced by trialkylphosphine ligands, it is possible to preserve the catalytic activity of the complex. Such a catalyst will selectively decarboxylate benzene polycarboxylic acids containing carboxyl groups on adjacent carbons to mixtures of isophthalic and terephthalic acids. Preferred solvents for this reaction are dioxane, acetone, and methyl-ethyl ketone. Reaction temperature is 200-220°C. By applying this reaction to a mixture of acids obtained by alkaline

¹⁶ Catalytic Hydrogenation of L. T. Tar Fraction.

¹⁷ Study of Fischer-Tropsch Process Using Nitrided Iron Catalyst.

¹⁸ Aliphatic Amines from Carbon Monoxide, Steam and Ammonia.

¹⁹ Decarboxylation of Coal Acids to Benzene dicarboxylic Acids by S. Friedman, S. R. Harris & Irving Wender, U. S. Bureau of Mines.

oxidation of coal, char or other coal derivatives, it is possible to obtain a product rich in isophthalic and terephthalic acids.

Using these data and others scattered in literature, the authors have been able to make projections of a process that can turn a ton of coal into about 400 lbs. of isophthalic and terephthalic acids with a value of 5 to 10 times that of the original coal.

The precipitated iron catalyst undergoes a series of changes, many of which are accompanied by heat effect during its preparation and in the course of F T synthesis. In his paper²⁰, M. Novohradsky of Fuel Research Institute, Bechovice (Czechoslovakia) has studied the intensity and character of the heat effect, velocity and time course of the changes in the catalyst, temperature at different stages, reversibility of the change, change of thermal conductivity of the catalyst, etc. by DTA after suitable modification. During the flow of various gases, viz. nitrogen, carbon dioxide and monoxide, hydrogen and synthesis gas, the thermal differences were measured. Also, the amount and composition of the inlet and outlet gases were measured.

The activity of iron catalysts used in this synthesis is influenced to a considerable extent by the method of its preparation. During the reduction stage, hydrogen reacts with oxygen of ferro-ferric oxide lattice with simultaneous increase of iron. Since the course of this process is slow, this does not show up as a good peak in the DTA curve. The course of reduction in this stage is however shown by a decrease in weight corresponding to the loss of reaction water which can be determined by thermogravimetric analysis. The formation of the catalyst at the start is a very complicated process accompanied by vigorous exothermic and endothermic reactions. The DTA results stress the importance of careful treatment before synthesis is started.

From the Planning and Development Division, FCI Ltd., five papers were presented, one²¹ of which dealt with the application of various gas chromatographic techniques which can be applied for the fractionation of hydrocarbons derived from coal and petroleum, according to boiling point, carbon number, retention index and structural types; the other 4 papers²²⁻²⁵ dealt

with physico-chemical studies on several catalysts—developed in this laboratory—used in shift reaction, carbon monoxide conversion and gas reformation, etc. These papers have been reviewed elsewhere (pp. 58-60) in this journal.

Session 3: In the process of coal carbonization, the by-products, viz. benzole, coal tar, liquors, etc., contain some of the important chemical compounds essential for the development of fine chemicals, pharmaceuticals, dyestuffs, plastics and food-processing industries. Considering 13.5 million tons/yr of coal carbonized in India at present, recovery potential of the major by-products can form the foundation of a full-fledged chemical industry. The coke production will tend to increase in future in spite of reduction in its rate of consumption/ton of pig iron produced; a corresponding increase in carbonization by-products is therefore expected.

In their paper²⁶, B. S. Filippov and V. S. Pospelov of the Institute of Fossil Fuel, Moscow have presented an analysis of the utilization of coal carbonization products in USSR. 37 per cent of the products goes to chemical industry, 30 per cent to non-ferrous metallurgy, 22 per cent to agriculture and 11 per cent to other branches. The main tasks of coking industry are to develop methods for the recovery of by-products, such as production of sulphuric acid and colloidol sulphur from coke oven gas hydrogen sulphide, cyanide and rhodamide from cyanogen having a concentration of 2 g/m³ of gas and use of coke oven hydrogen for ammonia synthesis. The authors have drawn attention to the problem of production and treatment of ethylene and other unsaturated hydrocarbons from coke oven gases and to the use of coal tar multi-ring hydrocarbons. In conclusion, they observe that the coal chemical and petroleum industries should complement each other.

S. K. Roy, G. S. Murthy and H. S. Rao (CFRI) have reported²⁷ the presence in significant proportions of

Catalyst by V. K. Puri, N. C. Ganguli & S. P. Sen [*Technol.*, 7 (1970), 59].

²³ Thermogravimetric Investigations on Reduction & Oxidation Properties of Reformation Catalyst by B. R. Arora, R. K. Banerjee, N. C. Ganguli & S. P. Sen [*ibid.*, 60].

²⁴ New Concept in the Field of Catalysts Based on Universal Spherical Wave Theory by S. P. Sen, B. Sen & D. K. Mukherjee, [*ibid.*, 60].

²⁵ The Nature of the Active Component in Copper Oxide-Zinc Oxide CO-Conversion Catalyst by P. K. Ghosh, J. S. Tiwari, S. C. Sinha, N. Roy & A. Sarkar [*ibid.*, 58].

²⁶ Some Data on the State & Outlook of Using the Coal Carbonizations Chemical Products in the USSR.

²⁷ A Survey of Industrial Coke Oven Benzoles: Their Composition and Utilizations.

²⁰ Differential Thermal Analysis of a Precipitated Iron Catalyst for the Fischer-Tropsch Synthesis.

²¹ The Application of Gas Chromatographic Technique to the Analysis of Complex Hydrocarbon Mixtures Derived from Coal & Petroleum by N. C. Saha [see *Technol.*, 6 (1969), 227]

²² The Effect of Thermal Treatment on the Physico-Chemical Parameters of Fe₂O₃ and Fe₂O₃ - Cr₂O₃ Type Shift Conversion

benzene (88 per cent), toluene (17), xylene (4) and cyclopentadiene (including dicyclopentadiene) 1 per cent in benzole and benzene forerunnings, obtained from high temperature carbonization plants. Carbon disulphide is the major constituent of benzole forerunning fractions boiling upto 80°C. The dicyclopentadiene and carbon disulphide contents of benzole forerunnings from Bhilai Steelworks are 12 and 4 per cent respectively. The main difference between the htc and ltc benzoles is the high olefinic content of the latter, which is about 30 per cent. The aromatic content of the latter is about 55 per cent while the rest are saturated hydrocarbons. The authors have discussed the utilization of the above-mentioned important chemicals as raw materials for the production of fine chemicals, pharmaceuticals, dyestuffs, plastics, etc. The following are some of the processes using toluene and xylene as raw material, developed at CFRI: (1) Benzaldehyde by catalytic vapour phase oxidation (with air) of toluene using catalysts like vanadium pentoxide or potassium sulphate-silica; (2) benzoic acid by catalytic vapour phase oxidation of toluene using metavanadate as catalyst; (3) disproportionation of toluene into benzene and mixture of *o*, *m* and *p*-xylenes using aluminium-silica as the catalyst.

R. N. Bhattacharyya, S. K. Roy and H. S. Rao²⁸ (CFRI) have stated that though htc and ltc tars contain 1.65-2 per cent methyl naphthalenes—now currently in demand—no commercial method for their recovery is available. Their potential recovery in India is about 9000 ton/yr (assuming the yield of tar as 8 gals/ton of coal carbonized by htc). They have surveyed²⁹ the alkyl naphthalene content of various coke oven products, viz. from Bhilai, Neyveli, Shalimar tarworks and CFRI pilot plants and described a procedure for their isolation using a combination of absorption spectroscopic and vapour phase chromatographic methods which comprise (1) making the tar oil neutral and collecting the fraction (2) distillation of the neutral oil and collecting the fraction having boiling range 238-246°C which contains mostly α and β methyl naphthalenes, (3) separation of α and β methyl naphthalenes by crystallization.

The drained naphthalene oils from Shalimar are a good source of the above two naphthalenes and might be commercially treated. Contrary to expectation, neutral oil from Neyveli ltc tar contains substantial

quantities of paraffinic hydrocarbons. The authors claim that the eutectic mixture of α (80 per cent) and β (20 per cent) methyl naphthalenes on cold (−20°C) pressing of the crystals from the neutral oil fraction (238-246°C) can be converted to 70 per cent β and 30 per cent α -isomers under fluidized bed catalytic conditions and this process can be used in conjunction with the isolation method so as to yield more of the β -isomer.

The paper²⁹ by M. B. Roy, P. K. Banerjee and C. S. B. Nair (CFRI) deals with studies on the utilization of ltc tar (fraction 230-300°C) as wash oil. They showed that low temperature neutral oils possess benzene absorption characteristics from gases comparable with those of conventional high temperature oil (230-300°C). The feed oil for these studies were prepared from tars obtained by the low temperature carbonization of coals from Talcher and South Balanda (Orissa). The tar oil fraction (230-350°C) freed from tar acids and bases, dried and fractionated and separated into the following 4 cuts, viz. 230-270°, 270-300°, 300-330° and 230-300°C; these fractions were tested for their benzole absorption characteristics.

As the major constituents of wash oil in the range 230-270°C, besides naphthalene and methyl naphthalene, are acenaphthalene and higher alkyl naphthalenes, the authors considered desirable to study the behaviour of representative member of this class as well of all the absorbent studied, the performance of α -methyl naphthalene showed the best absorption capacity; the aromatic—rich oil comes next. The aliphatic-rich fractions had the same absorptive capacity during the first hour but showed a fair decrease with time. The performance of other low temperature oils were intermediate between those of aromatic and aliphatic-rich oils. Being of low specific gravity, viscosity and solidification temperature, the low temperature oils should be more attractive for use in plant operation.

In the next paper³⁰, S. K. Mukherjee, P. K. Banerjee and C. S. B. Nair (CFRI) have studied hydroalkylation of motor benzole obtained as by-product during rectification of benzole for recovery of benzene, toluene and xylene by thermal dealkylation at atmospheric pressure. The fraction 110-115°C obtained on distillation of motor benzole from a commercial high temperature coke plant was used as a feed. Hydrogen was 99.6 per cent pure. The conversion was 82 per cent with selectivity upto 77.4 per cent in the optimum range 780-830°C, contact time 3-6 secs and hydrogen/feed ratio around 3. The authors have suggested the following two types of reac-

²⁸ Occurrence & Recovery of Alkyl Naphthalenes from Coke Oven By-Products.

²⁹ Utilization of Tar Oils from L. T. Tar & Wash Oils from Benzole Recovery.

³⁰ Hydroalkylation of Motor Benzole.

tions taking place: (i) $C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$; (ii) $C_7H_8 \rightarrow 7C + 4H_2$. The energy of activation for the benzene formation and overall reactions were found to be 51.05 and 29.36 k.cal./mole respectively.

The coke formation under optimum conditions were about 5 per cent w/w of feed and increased at temperatures beyond 830°C and/or with lowering H_2 /feed ratio. The yields of by-products boiling above xylene fraction was nearly 10 per cent v/v at hydrogen/feed ratio 1.5 and this reduced to 6 per cent of feed at higher ratios.

In the next paper, R. N. Bhattacharyya, S. P. Srivastava and H. S. Rao³¹ (CFRI) have studied dealkylation of alkyl naphthalenes in tar oils and drained naphthalene oils to naphthalene in the range 450-650°C using fixed and fluidized bed conditions in presence of alumina-silica and alumina-baria catalysts. In the fluidized bed operation at temperature 450-550°C, mostly isomerization reactions involving the transformation of 1-methyl naphthalene to the thermodynamically more stable 2-methyl naphthalene took place. Under fixed bed operation, the course of reaction was found different at high temperature (520-620°C). Naphthalene was the major product under these conditions and formed through the free radical mechanism.

A. N. Bose and A. K. Ganguli³² (CFRI) discussed their work on the production of naphthalene by catalytic hydrodealkylation of alkyl naphthalenes. The naphthalene oil fraction (225-260°C) after removing acids and bases was used as the feed. Cobalt-molybdenum on alumina and alkalized chromium oxide on alumina were found suitable as catalysts. The effect of temperature at initial hydrogen pressure 300 psig and reaction time 3 hr. showed that naphthalene formation was insignificant upto 475°C, thereafter conversion steadily increased reaching 38.3 per cent at 500°C when 1- and 2-methyl naphthalene showed sharp decrease with appreciable rise in naphthalene formation. The disappearance of the alkyl naphthalene, however, was not fully accounted by the formation of naphthalene indicating that the other side reactions involving alkyl naphthalenes had also occurred. 1-methyl naphthalene was more active than 2-methyl naphthalene. An initial pressure of 300 psig of hydrogen was optimum, while the percentage of conversion rose from 23 to 38.44 on using cobalt-molybdenum catalyst in alumina. The rate of formation of naphthalene was first order with respect to alkyl naphthalenes and 0.5 order with respect to hydrogen.

Subodh K. Roy, Sisir K. Roy and H. S. Rao³³ (CFRI) claimed to have produced α - and β -naphthaldehydes through vapour phase oxidation of α - and β -methyl naphthalenes at 250 and 400°C respectively. Using spectroscopic and gas chromatographic techniques quantitative values were obtained on product composition. Data on product distribution as a function of operating conditions are presented. Ferric vanadate catalyst was found most effective; the weight percentage yields were 50 and 34.5 for α and β methyl naphthalenehydes respectively. The oxidation of 2-methyl naphthalene to menadione—an anti-haemorrhagic agent used in medicine—has been studied and isolation of the product accomplished with above 40 per cent yield. The mechanism of the reaction has been explained by the process of chain reaction through dehydrogenation, peroxide formation and peroxide decomposition. The authors suggest the role of catalyst as catalyst donor and abstractor which thus helps to initiate the chain reaction.

D. K. Sen and C. S. B. Nair³⁴ (CFRI) found acetic acid a good solvent for the recovery and purification of naphthalene and anthracene from coal tar fractions. Using 90 per cent acetic acid and crystallizing from a solution under selected conditions, crude naphthalene could be upgraded to 99.7 per cent naphthalene content with an overall recovery around 90 per cent in one step using solvent to feed ratio 5:1. By proper reuse of the mother liquors and washings from one crystallization step to treat a fresh lot of crude cake, it was possible to further lower the solvent requirements considerably. This procedure has also enabled the recovery of naphthalene to be raised to around 95 per cent without any significant lowering in the purity level. Another group of solvents, known as 'Solvols' were found to be equally effective for this purpose.

Acetic acid could be used for upgrading of anthracene from crude anthracene cakes and oil. The high solvent requirements and the necessity to use acetic acid of different concentrations for the different steps, however, render the process less attractive. Admixture of some selected solvents with acetic acid enabled anthracene of more than 95 per cent to be obtained from a feed containing around 20 per cent anthracene in two crystallization steps. The solvent/feed ratio could be reduced to around 2 and the anthracene recovery increased to around 95 per cent by reuse of the mother liquors and washings.

³¹ Studies on Dealkylation of Alkyl Naphthalenes.

³² Hydroalkylation of Alkyl Naphthalenes and Denaphthalenized Naphthalene Oils from Coal Tar Sources.

³³ Catalytic Vapour Phase Oxidation of Monomethylnaphthalenes to Naphthaldehydes.

³⁴ The Recovery and Purification of Naphthalene & Anthracene from Coal Tar Oils.

C. S. B. Nair³⁵ (CFRI) has shown that many important chemicals and intermediates can be produced by the oxidation of coal tar based hydrocarbons under appropriate conditions. The production of phthalic anhydride by the catalytic oxidation of different feed materials, viz. naphthalene cake, crude naphthalene oil, naphthalene free oil, crude anthracene cake and solid-free anthracene oil has been studied in a fluid-bed reactor. A vanadia-based catalyst having the optimum size range—60 + 100 B.S.S. was found to be quite active with various tar oil feeds. The highest yield of phthalic anhydride from crude naphthalene oil was 46.7 per cent obtained at 400°C and air space velocity 4056 l. air/hr l. cat. The conversion varies linearly with naphthalene content of the tar oils. With crude cake, the production of anhydride reaches the maximum value of 79.2 per cent within 380-410°C. Other feed materials gave lower yields.

The purification of the product—effected by rectification under partial vacuum—is essential for obtaining high grade phthalic anhydride. Considering all these factors and as the price of naphthalene oil is 25-30 per cent that of naphthalene, the author observes that naphthalene oil containing more than 40 per cent naphthalene is a promising additional raw material for phthalic anhydride production.

Of a large number of catalysts studied for the vapour phase oxidation of anthracene to anthraquinone, the most promising conversion, 85 per cent, was obtained with a catalyst comprising vanadium pentoxide-ferric oxide-potassium sulphate and silica developed at CFRI, according to C. S. B. Nair and A. K. Ghosh³⁶. The effect of variables, like temperature of catalyst, space velocity of air, anthracene/air ratio, contact time and various treatments of catalysts have been investigated. The catalyst was quite active after 200 hr. of use and the attrition loss over this period was 0.0057 g/g. of cat./hr. of fluidization pointing to a catalyst replacement time of 3 years.

The feed for these studies consisted of refined anthracene of 93 per cent purity. The experimental results showed that selectivity to anthraquinone was around 90 per cent at feed rates above 60 g./hr/l. cat. at 420 and 450°C. This decreased at 490°C to 82-84 per cent over the feed rates studied viz. 40-160 g./hr/l. cat. The conversion was in the range 90-92 per cent at temperatures above 440°C.

The yield of anthraquinone was almost directly proportional to anthracene content of the feed. The overall conversion of anthracene as well as conversion of anthracene to anthraquinone, phthalic anhydride and carbon dioxide have been found to have a first order dependence on the anthracene concentration. The mechanism of conversion is possibly through the formation of endocyclic peroxides in one case and intermediate compounds like 9-hydroxyanthracene and 9, 10 dihydroxyanthracene in the other.

In their paper³⁷, O. K. Guha and A. C. Bhattacharyya (CFRI) claimed to have developed a rapid isothermal gas chromatographic analytical method for anthracene present in a mixture of phenanthrene-anthracene and carbazole with a 2 m. long column packed with 30 per cent cadmium chloride or acid washed indigenous super-insulation brick of —60 + 80 mesh size. The column was suitable for the rapid analysis of mixtures of condensed aromatics under programmed temperature condition and showed stable performance for a long period.

Session 4: In the first paper³⁸, the author (C. V. S. Ratnam, Neyveli Lignite Corpr.) describes in details the working of the large low temperature carbonization plant (which includes a briquetting plant also) in the giant integrated lignite project at Neyveli. The other units in this project are a thermal station and a urea plant. The briquetting and carbonization plant, the biggest of its kind in the east, besides producing smokeless lt. coke, known as 'Leco', and charfines. The tar products unit comprises 5 sections with arrangements for recovery of phenols and their purification. From gas liquor phenol is separated by extraction with sodium phenolate and isopropyl ether. The raw phenols are subsequently treated in a phenol separation plant followed by distillation. The following tar products are being manufactured: carbolic acid, which is chemically pure and suitable for phenol formaldehyde resin, meta-paracresol mixture, xlenols, orthocresol and multi-valent cresols. The problems encountered in the operation of the tar products unit and their solution are discussed in details. The design and installation of an additional unit for making catechol cut, heavy boiling cut and multivalent phenol residue are described.

In the next paper³⁹, Subodh K. Roy, G. S. Murthy and H. S. Rao (CFRI) have identified coal tar bases

³⁵ Production of Phthalic Anhydride by Vapour-Phase Oxidation of Coal Tar Oils.

³⁶ Catalytic Vapour-Phase Oxidation of Anthracene to Anthraquinone.

³⁷ Rapid G. C. Analysis of Phenanthrene-Anthracene Carbazole Mixtures.

³⁸ Manufacture of Various Types of Phenols from Lignite Carbonization.

³⁹ Nitrogenous Bases from Lignite Carbonization By-Products.

such as pyridine, quinolines, etc. in the E.G.R. (first condensate) and middle oil obtained from ltc at the Neyveli Lignite Project. The authors have shown that low boiling tar bases specially β -picolines are present in appreciable amounts in the middle oil fraction and suggest that their recovery can be an economic proposition.

The weight of distillate boiling upto 270°C constitutes 18 per cent of the E.G.R. tar, while it is 84.5 per cent in middle oil. The base contents of distillate boiling upto 270°C is 0.39 per cent only in E.G.R. tar compared to 1.84 per cent in the case of middle oil proving thereby that the middle oil contains most of the low boiling tar bases.

The middle oil (B.P. range 295°C) was chemically treated to recover the crude tar bases, which were then fractionated in a whirling heliband column to obtain 14 fractions boiling upto 180°C. The residue was fractionated under reduced pressure to obtain 7 fractions boiling between 180 and 260°C. These fractions were individually examined by measuring densities as well as by ultraviolet and infrared spectra. The identification of the individual bases was carried out by comparing their i.r. spectral frequencies against the diagnostic frequency bands of the authentic samples, quantitative analysis being done by the base-line procedure. 32 components were identified—15 pyridine and its alkyl derivatives, 4 anilines and 13 of the quinoline and isoquinoline group.

Pyridine bases accounted for more than 50 per cent of the total bases, rest being quinolines and their derivatives. Among picolines, β -picoline was the predominant and α -picoline the least abundant. Among the dimethyl pyridines only 2-4 and 2-6 lutidines were identified and only one trimethyl pyridine 2-4-6 has been identified. A number of ethyl methyl pyridines have also been identified and no pyridine derivative with alkyl chain length greater than 2 carbon atoms was detected except 4 isopropyl pyridine.

The authors have presented a comparative study of the distribution of individual tar bases in the middle oil and light oil fraction of tar obtained from Neyveli as well as from ltc (CFRI) and htc (Rourkela) of coals from which they conclude that Neyveli tar constitutes a better feedstock and is particularly rich in β -picolines.

O. K. Guha, A Bhattacharjee and P. K. Banerjee⁴⁰ (CFRI) have described a new method for the analysis of

phenol, *o*-, *m*- and *p*-cresols present in ammoniacal liquors by counter-current distribution technique, since the conventional methods, viz. solvent extractions followed by fractionation and estimation, tend to affect the original composition and column chromatographic methods are more suitable for the estimation of dihydric phenols only.

The above method involves quantitative recovery of monohydric phenols by steam distillation followed by estimation of individual components. Known amounts of the steam distillate were charged into an 100 all-glass tube (CCD) apparatus and 80 transfer are effected for the effective fractionation between the phases, viz. cyclohexane and 0.1 per cent aqueous salt solution; the u.v. absorbance of the cyclohexane phases of each tube were taken at 279 and 274 m μ and the individual components were estimated from the reading of 5-6 consecutive tubes around the peak tube. The resolution of the absorbances of the binary mixtures with overlapping bands was done by means of a simplified formula developed by the authors. The method has been verified with synthetic mixture and 3 ammoniacal liquor samples obtained from 3 different sources.

T. J. Bhaduri, D. K. Sen, K. K. Tiwari & C. S. B. Nair⁴¹ (CFRI), after surveying the solvent extraction methods of recovery of tar acids using various solvents carried out at CFRI, described their work with solvents, like acetic acid, acetamide and ammonia solution, for recovery of tar acids from ltc tar fractions (boiling upto 270°C). The disadvantages of the conventional method, viz. using caustic soda followed by acid regeneration, have been pointed out.

The usual composition of the fractions was tar acids 42-45 per cent, tar bases 4-5 per cent and neutral oil 50-54 per cent and most extractions have been done in separating funnels of jacketed column provided with thermostat and axial stirrers.

The authors have discussed the relative efficiency of different solvents, studying in all cases process variables, like solvent concentration, feed/solvent ratio and operating temperature. The extraction capacity of acetic acid increased with increasing concentration reaching a maximum at 60 per cent acid. In the case of acetamide, saturated solution gave the best extractive capacity. In case of ammonia, a 4 per cent solution gave the best extraction. A 2-stage extraction with acetic acid yields 89.45 per cent tar acids and with saturated acetamide 90 per cent extraction was obtained. Recovery of tar

⁴⁰ Separation & Quantitative Estimation of Lower Boiling Monohydric Phenols Present in Ammoniacal Liquor.

⁴¹ Recovery of Phenols from Coal Tar.

acids from the extract phase was done by fractional distillation.

P. N. Mukherjee, J. N. Bhowmik, K. N. Ray, I. B. Paul and A. Lahiri⁴² (CFRI) have shown that phenols and tar acids mixture can be utilized for the production of anion-exchange resins, which are extensively used for demineralization of water. In the preparation of these resins condensation as well as Mannich reaction most probably occur simultaneously leading to the formation of the cross-linked polymer. They have used a mixture of pure phenol and formalin in the molal ratio 1:0.8 and heated on a water bath till condensation proceeded. It was then dissolved in ethylene-diamine hydrate (1 mole) followed by addition of 2-2 moles of formaldehyde. The reactants were then allowed to condense at 90°C for 2-3 hr. and finally set at 100°C for 144 hr. The method was later modified and the product had an exchange-capacity of 500 me/100 g.; its performance was fairly good, better than that of De-Acedite-G—a commercial product with satisfactory regeneration efficiency and swelling characteristics. However, the resin deteriorates after a few cycles of operation in a column; this defect is now being rectified.

S. Hussain, P. A. Swaroop, A. Vijayasarithi and D. P. Agarwal⁴³ (RRL, Hyderabad) have chlorinated xylenols and tar acids present in ltc tar obtained from lignite carbonization and obtained products having a Rideal-Walker coefficient of about 175 which can be effective substitutes for the imported chloroxylenols. Their other findings are: (i) xylenols are 6 times more powerful than phenols as bactericidal agents; (ii) *p*-chloroxylenols are more active than *o*-chloroxylenols; (iii) the new compound, 4-6 dichloro 2-3 xyleneol, prepared by them has a great potentiality in the formulation of antiseptics.

C. S. B. Nair and D. K. Sen⁴⁴ (CFRI) have studied the possibilities of utilizing crude tar acids obtained from htc, ltc and lignite tar for the production of formaldehyde condensation resins, which may be used for the manufacture of hard boards, plywood, etc. They have developed a process for the preparation of water-soluble resins by properly adjusting the proportion of tar acid, formaldehyde and the catalyst (caustic soda) and reaction temperature, time and pressure. Tar acids were obtained

from coal tar fractions boiling upto 270°C by alkali extraction followed by acidification. These contain 45-50 per cent of the tri-reactive phenols. The properties of the resin prepared using different molecular ratios of tar acids, caustic soda and formaldehyde have been studied. High alkali concentrate ion resulted in the formation of sodium salts of the phenol alcohols, which remained in solution. At the same time, it was possible to obtain water-soluble resins at alkali concentration as low as 0.1 mole/mole of tar acids with higher proportion of formaldehyde. Resin prepared with high alkali concentration could be stored for longer time, while that prepared at low alkali concentration can be used directly for bonding and impregnation purposes. The authors claim that these resin solutions may be conveniently used for bonding of various materials, like saw dust, bagasse, cotton waste, jute waste, etc. for making boards. This process is claimed to have commercial possibility.

Sisir K. Roy, P. Bhattacharyya, G. S. Murthy and H. S. Rao⁴⁵ (CFRI) have shown the possibility of converting picolines, obtained as by-products from coal tar fractions, to cyanopyridines through ammoxidation in the presence of a suitable catalyst. The cyanopyridines could in turn be hydrolysed to the corresponding carboxylic acids and amides which are the starting materials for manufacturing various drugs. They have studied the production of 4 cyanopyridines from 4 picolines and 3 cyano-pyridines from 3 picolines by ammoxidation in a fixed bed with various catalysts over a wide range of operating variables like temperature, air/picoline ratio, ammonia/picoline ratio and load on catalyst. The products have been identified and estimated by i.r. spectrophotometry. The optimum conditions for the production of 4 cyanopyridines have been given. The catalysts were found to retain their activity for 100 hr. but regeneration was easily done by air at 400°C. The mechanism of the ammoxidation reaction has been discussed, and the authors propose the production of nicotinic acids by this route.

Sisir K. Roy, P. Bhattacharyya, H. S. Rao and A. Lahiri⁴⁶ (CFRI) suggested a scheme for commercial utilization of the aromatics as well as nitrogen heterocycles present in coke oven by-products. Exhaustive studies on aromatic hydrocarbons, viz. toluene, xylene, naphthalene and its alkyl derivatives, indicate that by ammoxidation, these compounds can be converted to

⁴² Anion-Exchange Resin from Tar Acids, Phenols, Cresols and the Like.

⁴³ Production of Chlorinated Tar Acids for Use as Disinfectants.

⁴⁴ Production of Formaldehyde Condensation Products from Tars and their Utilization in the Manufacture of Hard Boards, Plywood and Moulded Articles.

⁴⁵ Catalytic Vapour-Phase Ammoxidation of Monomethyl Pyridine to Cyanopyridines.

⁴⁶ Ammoxidation Route to Nitriles.

Symposium, Seminar, Lecture, Etc.

Chemicals and Oil from Coal

An international symposium on chemicals and oil from coal was held during December 6 to 8, 1969 at the Central Fuel Research Institute (CSIR), Jealgora, Dhanbad, which was inaugurated by Dr. V. K. R. V. Rao, Minister of Education and Youth Services, Government of India. In all 62 papers were presented and discussed. Of these 18 were by foreign scientists representing some of the well-known institutions like the Office of Coal Research, Washington, Pittsburgh Coal Research Centre (U. S. Bureau of Mines), Pennsylvania, Australian Coal Industry Research Laboratories, Universities of Utah (USA), Sheffield, Birmingham and Hokkaido (Japan), Institute of Fossil Fuel, Moscow, Fuel Research Institute of Czechoslovakia, Institute Für Technische, Berlin (W. Germany), Department of Mines, Energy & Resources, Canada, Heinrich Koppers, etc. Six papers were contributed from the Planning & Development Division of Fertilizer Corpn. of India.

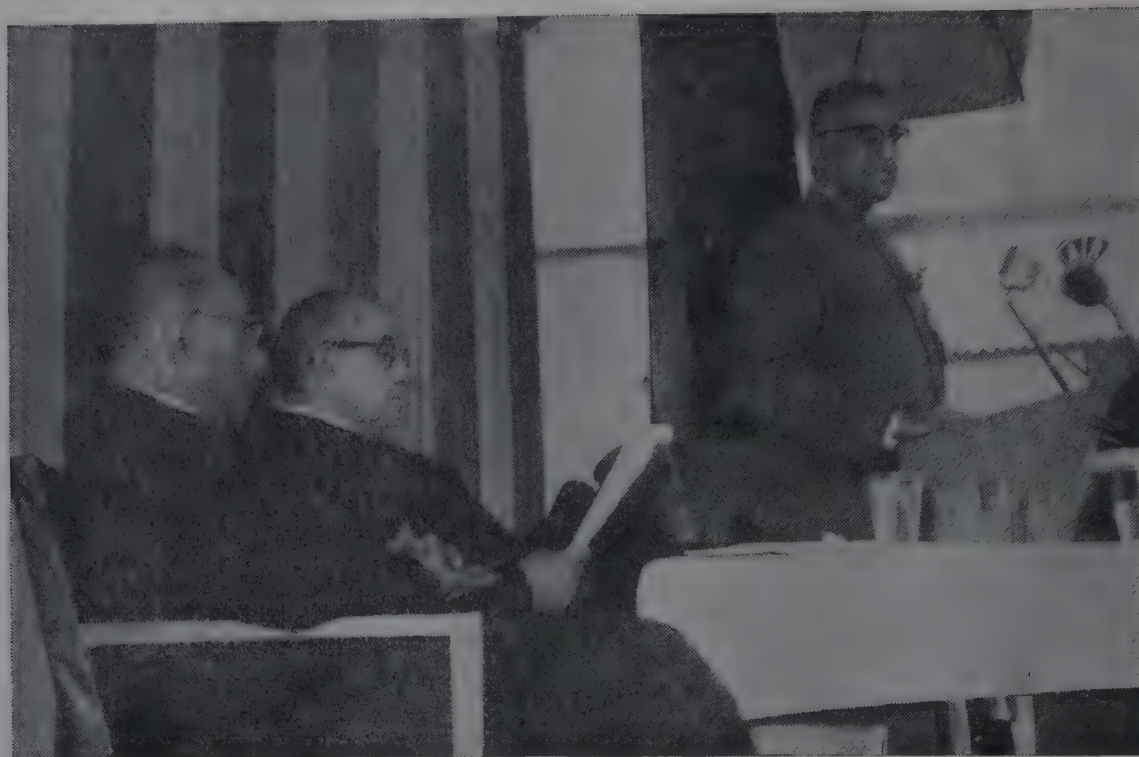
In welcoming the delegates, among whom there were some distinguished foreign scientists too, Dr. Atma Ram, Director-General CSIR, said that the potentials of chemicals from coal are great. Fortunately, we have large reserves of coal in India while the present proved reserves of crudes are not more than 100 million tonnes, which is obviously too meagre. But the hunger for oil is growing and in some countries the use of oil and gas has dwarfed all other sources of energy. It is estimated that India may consume 110 million tonnes of petroleum products by the end of this century. Since one ton of coal is capable of producing 0.33 to 0.50 ton of oil, it is worthwhile undertaking a programme of research and development on the processing of coal for oil for which a beginning can be made with the Assam coals. Dr. Atma Ram pointed out that CFRI was the moving spirit behind the 1948 and 1958 studies on production of oil from coal. He was gratified to note that CFRI is reviving the interest of the country in this subject once again and hoped that perhaps by 1978 the first major plant for conversion of coal to oil will be commissioned in Assam.

Sir Jehangir Ghandy, Chairman, CFRI Executive Council, in his presidential address, said that traditionally it is coal which gave rise to the synthetic chemical

industry based on hydrocarbons, especially aromatic hydrocarbons. It is the by-products of coal carbonization, like benzene, toluene, naphthalene, phenols, tar bases, etc., derived mainly as by-products of steel industry, which triggered off the 'Chemical Age'. In due course, the steel industry in most countries reached a saturation level or even when steel production increased, the expansion of the coal carbonization industry did not keep pace with it because of the economics effected in the consumption of coke. As a result, coal could no longer satisfy the needs of the chemicals industry which had its origin as a by-product utilization scheme. So, during the World War II and after, petrochemicals came to the fore. During this war, coal was used as a source of oil by hydrogenation and chemicals in Germany. However, in the post-war era only one plant, viz. at Sasolburg (S. Africa), came into existence where commercial production of both oils and synthetic chemicals is done. It is now a successful venture and is being expanded. In the USA, following a review of the resources position by the President's Material Policy Commission, effects were being made especially under the aegis of the U.S. Bureau of Mines to break new grounds and for nearly 25 years basic and plant-scale research has been carried out in exploring all possible routes of conversion of coal into oils and chemicals. Anxious about its ever-increasing needs for energy and chemicals and continued exhaustion of its home resources of petroleum and gas, USA is spending vast sums for conversion of coal into oils and have set up for that purpose a separate organization, the Office of Coal Research (OCR).

CFRI has estimated that the requirements of energy in India by the end of this century will at least be equivalent to 1000 million tons of coal; of this perhaps 1/3rd will be oil products required to meet the mobile energy needs. The gap between the indigenous production and demand will therefore have to be met by imports or synthetic liquid fuels from coal.

Inaugurating the symposium, Prof. V. K. R. V. Rao, Minister for Education & Youth Services, Government of India, said that coal certainly assumes a special interest in India as an alternative to oil both for energy as well supply of basic intermediates for the chemical industry. He opposed the traditional thesis that coal is



Dr. V. K. R. V. Rao, Union Minister of Education and Youth Services, Inaugurating the Symposium on Chemicals and Oil from Coal on Dec. 6, 1969 at CFRI. Seated (left to right) are: Dr. A. Lahiri, Director, CFRI, Sir Jehangir Ghandy, Chairman, Executive Council, CFRI and Dr. Atma Ram, Director General, CSIR.

totally uneconomic as a raw material for the production of oils, as it ignores the likely improvements in its technology. It also ignores other important factors, such as values attached to foreign exchange, the very large employment potential in the mining of coal and the defence aspect in continuing to rely so heavily on imported crude oil. He urged that the techno-economic accessibility of utilizing coal to manufacture oil must be studied afresh and in this connexion mentioned CFRI's patent on production diesel fuel and high speed diesel oil from coal tar fraction, including development of an indigenous catalyst for the process which holds promise.

Dr. Rao mentioned that there are several chemicals which can best be manufactured from coal only while there are others where competition with other raw materials is possible but our demand for these chemicals will increase so rapidly that even with the estimated availability of alternative raw materials, coal will continue to be an important raw material for a number of chemicals. In this connexion he mentioned the establishment of 3 large coal-based fertilizer plants.

Dr. E. E. Donath, one of the greatest living experts who worked in Germany during and before the war on coal conversion, and whose services have been loaned to India by US Agency of International Development, traced briefly the background of the work on synthetic fuels from coal in Germany and USA. Conversion of coal into oil by hydrogenation at high pressure and

temperature was developed to full commercial scale in Germany before World War II; during the war, 12 commercial plants were in operation, which supplied the bulk of the aviation gasoline. The other products were jet and diesel fuel from brown coal tar, paraffin wax and lubricating oil. The cost of gasoline from coal was about 50 per cent higher than petroleum from a plant of 10,000 barrels/day. In these plants, a 2-step process was used; in the first phase, coal was mixed with recycle oil and made into a paste with finely divided low cost iron oxide as a catalyst. This paste was pumped at a high pressure with hydrogen into high pressure reactors at elevated temperature. There coal was reliquefied by additional hydrogen. The light oil was distilled into the desired fraction and further treated. From the heavy oils containing the coal ash, the latter was removed and the oil recycled and used for making new coal paste.

In the second stage, the coal and oils were converted into suitable final products of the desired hydrogen content and boiling range using hydro-refining and hydrocracking catalysts. At this stage, sulphur, oxygen and nitrogen were removed completely and stable fuels obtained.

U.S. Bureau of Mines had done independent research and development in the above field and was authorized to build a coal-hydrogenation demonstration plant utilizing the then available German technology. In this plant from 1950 several American coals were tested and

found suitable for conversion to oil. Since then developments in petroleum refining and in ammonia plants indicate areas of major improvements which can be applied to the classical coal hydrogenation process: (i) *Process Improvements*—the use of better catalysts leads to higher yields, conversion per-pass and lower hydrogenation consumption. This permits operation at lower pressure and reduces capital investment cost; (ii) *Equipment Improvements*—larger reactors, centrifugal compressors and pumps, lower cost heat exchangers lead to the lower capital investment cost connected with the use of large single units; (iii) *Operating Improvements*—more reliable and longer life armatures and automatic controls permit operation closer to optimum conditions and coupling of the process steps without intermediate let-down and tankage, thus reducing operation cost. (iv) Having taken advantage of all these developments, OCR sponsored projects and improved and modernized the coal hydrogenation process, as a result of which it now appears that cost of synthetic gasoline is near to that of the gasoline from petroleum in plants with a capacity around 30,000 to 1,00,000 barrels/day.

The primary product from the above processes is a synthetic oil containing 80 per cent middle distillates. After refining by hydrotreating, major fractions are kerosene, jet and diesel fuel. Dr. Donath expects that hydrogenation of Assam coal will lead to similar products, and sulphur will be removed as hydrogen sulphide. The presence of natural gas near the coal deposits will be of additional advantage as a source of hydrogen. The Assam crudes will also require hydrotreatment for their conversion into middle distillates with a high yield. Savings will result from a combined hydrotreatment of coal and crude oil fractions. Such a combined coal-oil refinery in Assam can supply a wide variety of chemical raw materials and intermediates, such as aromatics, phenols, tar bases, ethylene, propylene, etc.

The symposium was divided into the following 5 technical sessions: (i) Oil from Coal: Status of Art and Techno-economic Feasibility; (ii) Hydrogenation of Coal, Liquid Hydrocarbons and Carbon Monoxide; (iii) Recovery & Utilization of Tar Oils, Benzole Naphthalene and Anthracene; (iv) Recovery and Utilization of Phenols and Tar Bases, and (v) Direct Conversion of Coal.

Session 1: In the first paper¹, the author, George Fumich Jr., gave a brief account of the activities of the

¹ Projects on Coal to Oil and Other Energy Products under the Office of Coal Research.

Office of Coal Research of the US Dept. of Interior. It was created in 1960 to encourage and stimulate the production and conservation of coal by authorizing contract from coal research. Thus, projects on coal research supported by OCR have been conducted by independent research institutes, private industry and the universities. Most of the OCR projects have originated from unsolicited proposals. If on evaluation such a proposal is found workable within available funds, a contract is executed. Generally the work is applied development directed towards a practical commercial application within a reasonable length of time. Generally, a project begins with a laboratory-scale investigation, proceeds to a large bench-scale and may culminate in the construction and operation of a pilot plant. A final report describing the process in detail accompanied by designs of commercial equipment and estimates of commercial feasibility is then published and made available to all who are interested. So far, OCR has undertaken a major programme aimed at developing processes for manufacturing a natural gas substitute (essentially methane) and a major programme aimed at synthetic petroleum. A third important programme is the generation of electrical energy from coal because the threat of competition of nuclear power does exist. A great deal of coal will continue to be burnt for power generation in the foreseeable future and more efficient power systems would have the additional important benefit helping solve serious air and thermal pollution systems.

The author gave brief outlines of the scope of their activities on the following main projects: (1) **Pipeline Gas** (i) *By hydrogasification by the Institute of Gas Technology*: Detailed designs having completed, construction has been started; projected gas cost is 40 cents/1000 cu./ft but later study has shown further cost reductions. IGT is also proceeding on large bench-scale development of the electro-fluid bed process of production of hydrogen from char. (ii) *By Carbon dioxide Acceptor Process*: This project relates to the use of North-western lignite, its main feature being that it does not require pure oxygen. Dolomite is the heat-transfer medium and carbon dioxide absorber. Construction of a pilot plant began in August 1969. (iii) *By Bituminous Coal Research Inc*: The first phase of the work was a study of all known methods of coal gasification, on which a useful report has been published. The second stage is a 100 lb/hr. gasifier, which is now under operation. (2) **Computer Optimization of Gasification Processes**: Using sophisticated mathematical computer techniques, a number of investigations have been started to define and interrelate the important parameters of various

gasification systems. The computer programme will form a basis for determining the effect of coal cost and rank, estimated capital and operating costs of the gasification plants and by-products credits on potential commercial gas price. (3) **Gasoline Project:** Development of a process based on solvent extraction operation of coal and then to hydrogenate the extract to produce a refinery feedstock, a suitable source of high-octane gasoline. After completing the bench-scale work, the contractor, M/s Consolidated Coal Co., erected the pilot plant and started operating the extraction and hydrogenation sections in November 1966 and Feb. 1967 respectively. A zinc-chloride catalyst system promises to reduce commercial production cost. (4) **Char Desulphurization:** The contractor—FMC Corpr—has produced and successfully run a multi-stage fluidized-bed pyrolysis process having 100 lb/hr. coal throughput capacity. Commercially feasible yields of oil, gases (hydrogen and high Btu fuel gas) and char have been obtained. Extensive bench-scale experimentation is proceeding on char-desulphurization process which holds promise of being a source of low-cost and low-sulphur fuel for power generation. (5) **Project Sea-coke:** It has possible economic feasibility of simultaneous fluid-coking of coal mixed with residuum from petroleum processing. The purpose was to develop a process for using and treating coal in oil refinery fluidized coking units. The lighter fractions of coal would be converted to a refinery feedstock and the residual char could serve as a boiler fuel. (6) **H Coal Process:** It is an adaptation of the Hydrocarbon Research Inc.'s process based on conversion of coal in an ebullating bed to synthetic crude oil followed by additional treatment to refined products. Detailed studies based on 200 lb/hr. of coal indicated potential commercial feasibility in several coal-producing areas of USA. (7) **Electrogas dynamics (EGD):** A method of direct power conversion. Gases laden with coal-ash particles are expanded through channels resulting in work done which is collected as high voltages on an electrode at the downstream end of the channel. (8) **Low Ash Coal:** Technical feasibility has been demonstrated on lignite to coal by a solvation process for removing ash. The end-product, containing about 16000 Btu/lb has potential as power plant and gas turbine/diesel fuel, and as electrodes. (9) **Induction Heating of Coal:** For determining whether useful chemicals could be produced by electroprocessing of coal. (10) **Multiple Catalyst Fluidized Reactions:** Intended to explore the reactions of coal or char with steam in a fluidized bed in presence of several catalysts simultaneously at pressures up to 30 atm. (11) **Acetylene from**

Anthracite: The objective is large-scale manufacture of acetylene and other gaseous products. (12) **Fly Ash Construction Material:** Mixing fly ash with bottom slag or ash in predetermined amounts and adding small quantities of sodium silicate as binder. This mixture is pressed into shape and fired.

W.A.O. Hermann², with his experience of war-time German plants and conversant as he is with current technology in production of liquid fuels from coal, compares the influence of various factors on the costs of coal hydrogenation and reviews its prospects in perspective to the resources of coal in various countries and demands of energy.

The oil reserves of the world and of N. America, in particular, relative to the rate of consumption will not increase for ever. Even at present increasing expenditures for explorations and processing of crudes can be noticed. Contrary to the developments in Europe, the unit heat with oil in N. America costs still about 3 times as much as with coal. This price difference and the increasing costs to produce and process the petroleum provide the incentive to consider coal as an alternative raw material for production of liquid fuels and chemicals. Therefore, large oil companies in USA are acquiring coalfields and are investigating improved processes of coal hydrogenation.

Hermann traces the history of development of high pressure coal hydrogenation in Germany from 1926, when I.G. Farben-industrie negotiated substantial financial concessions from the Government for commercial scale demonstration using small reaction vessels of 0.6 m. I.D. (230 kg./cm²). Between 1936 and 1943 a dozen plants were set up with capacities upto one MMT/yr gasoline. The economies of small coal hydrogenation plants were sought to be improved by integrating with manufacture of synthetic rubber and chemicals. Acetylene and hydrogen were produced from off-gases and hydrogen returned to the fuel plant. In German plants hydrogen cost was more than 50 per cent of total production costs of gasoline. The chemistry and technological problems in coal hydrogenation are then discussed. The coal-oil paste has to be preheated which has its limitations and in the reaction vessels the heat of reaction has to be controlled by addition of hydrogen, the heat of reaction rising exponentially from 350 at 450°C to 550 kCAL/kg. at 490°C at 700 atm. The heat of reaction developed for lignite is considerably higher than for bituminous coals and is also higher with better catalysts.

² Oils and Basic Organic Chemicals from Coal by Hydrogenation.

The author also subscribes to the hydrogen transfer mechanism via vehicle oil and generally deprecates solvent extraction as the first step. The choice of vehicle oil composition was stressed. He discussed typical flowsheets of German plants for hydrogenation of low and medium oil bituminous coals to aviation fuels. Hydrogenation was carried out in two phases—the liquid phase at 700 atm and the vapour phase treatment in two stages at 300 atm. For a ton of gasoline, 1.84 tons of coal and 0.229 ton of hydrogen are required, hydrocarbon gases supplying about 44 per cent of hydrogen. Higher throughputs are achieved by diluting the paste oil with high boiling middle oil, thus reducing the viscosity and increasing heat transfer. The throughput increases to 0.6 ton maf coal/m³, reaction volume compared to 0.309 ton/m³ in the second and 0.396 ton/m³ in the first flowsheets. Surplus middle oil was thus produced; desired cracking achieved with less gas formation (50 per cent against 93 per cent) and 15.4 per cent hydrogen consumption against 24.8 per cent. The flowsheet was also recommended for extraction of tar acids, but the product in the vapour phase required more hydrogen. For vapour phase hydrogenation, products generally boiling below 360°C from the first stage reaction at 700 atm. and about 330°C from the 300 atm. liquid phase reaction are used. The vapour phase reaction was done either in two stages, 300 or 700 atm. Tungsten disulphide and 10 per cent tungsten on alumina are used for elimination of hetero-atoms and saturation of double bonds. Catalyst life of 3 years for saturation system and 1.5 years for the splitting system has been reported. The higher the asphaltenes and oxygen-containing bonds, the higher is carbon deposition on catalysts. Catalyst life is shorter with higher operating temperature, gas formation and hydrogen consumption. The difference in catalyst concentration in liquid and vapour phases are correlated with the severity of cracking, molecular weight, hydrocarbon gas formation and hydrogen consumption.

The economics of coal hydrogenation has been discussed in relation to the small German plants (5000-8000 bbl/day) compared to modern refineries (40,000-250,000 bbl/day). In the light of these, the possibility of Ebasco and Bechtel computation for an 1,000,000 tons/yr. plant being reduced is discussed. With multilayer vessels and much higher reactor volume, there could be an overall savings in capital investments and hence on capital charges, which was estimated at \$ 1.91/bbl. Saving in costs in high pressure vessels by reducing the number of units through increased capacity will effect correspondingly much larger savings in the rest of the plant.

Costs of production and compression of nitrogen are the next items for possible savings.

From coal and oil hydrogenation processes, some variants or newer processes have been developed, when the demand for higher octane gasoline rose. DHD process operates at 500-520°C and 30-50 atm. and the hydroforming process in Leuna at 10-15 atm. Variants and combinations of these 2 processes are the catalytic reforming, the hydrodealkylation at 50 atm. hydrocracking at 200 atm, icomex and the uncracking processes, the H. oil process and others. Techniques of precipitating catalysts giving high reactivity, use of catalyst is ebulliating bed, possibilities of eliminating vapour phase by using Combi process with nitrogen resistant catalyst at high pressure followed by vacuum stripping and alkali scrubbing can make a 30 per cent saving in cost of gasoline production.

However, the major scope of saving and credits lies in the recovery of by-products and chemicals which include sulphur, ammonium sulphate, phenols, cresols, xylenols, tar bases, aromatics, ethyl benzene and processing C₁ to C₄ hydrocarbons for production of ethylene, propylene, butylene, isobutylene and acetylene; possibility of production of oxo-alcohols from higher molecular olefines from middle oil is there.

Hermann concludes that fuels and chemicals can be made by high pressure hydrogenation from coal at prices competitive with those achieved by standard oil refining if the price ratio of coal to petroleum remains as at present and if all the improvements developed after the war are incorporated in the operating scheme and equipment of coal by hydrogenation and if larger equipment are used to reduce investment maintenance and heat costs.

In the next paper³ W. Jackh of Koppers reviews the shortcomings of the war-time coal and tar hydrogenation plants in Germany and discusses developments which may make such a plant economically viable. The pertinent points, in addition to the cost of coal, which affect the cost of the process are: production of cheap hydrogen; removal of inorganic substances, ash, etc; high pressure apparatuses. He concedes the USA with its stable low coal price (\$ 4/ton) and higher ex-refinery prices of liquid fuels has a better chance than European countries for converting coal either to liquid fuel or gas. The German war-time cost of hydrogen from coal was 4 Pfennigs/Nm³ of hydrogen. With coal at DM 60/ton, this figure will now be around 10 pfg/Nm³ but in large

³ Problems involved in the Hydrogenation of Coal.

plants (with say, coal throughput 5 million tons/yr), the cost is estimated at 3 pfg/Nm³. The developments mentioned by him in USA relate to production of pipeline gas by synthesis of methane. All the processes for hydrogen involve hydrogasification route. After reviewing the hydrogen production costs from different sources like heavy residues, naphtha, etc., he concludes that natural gas at American price (35 c/m³ MM Btu) produces cheapest hydrogen (3-4 pfg/Nm³) at 25 atm compared to naphtha (at 4-5 pfg/Nm³ at 25 atm.).

For removing ash from hydrogen, he proposes two routes, viz. (i) solvent extraction and (ii) BASF process of separating unreacted material from the liquid phase hydrogenates, both requiring novel, expensive measures which are a burden on the economy of the process. He suggests to choose a catalyst which will give the maximum conversion of coal in liquid phase and the importance of choice of low ash coal in order to reduce the residual sludge that has to be worked up.

Reactors of 200 cu.m. volume are now in commercial operating at 200 atm, which reduces substantially capital costs of processing plants. The construction of larger machines, higher capacities, improvement in equipment for heat transfer and exchange automation and monitoring of high-pressure circuit have considerably improved the prospects of coal hydrogenation. While the possibility of production of gasoline from coal in Germany is ruled out, in USA the process has possibilities with present cost of coal using natural gas as a source of hydrogen in plants of about 4 million tons of gasoline per year.

In their paper⁴, A. Lahiri and D. K. Mukherjee (CFRI), after a detailed review of all the methods of conversion of coal to oil, have discussed the economics of conversion of Assam coals to oil and chemicals. Of the 3 approaches, viz. pyrolysis route, direct hydrogenation of coal route and Fischer-Tropsch synthesis, the first has prospects for limited production of oil in large integrated plants where char will be used for power generation and gas and tar for oil and chemicals production. But there does not appear to be any development of char-fueled boilers and pyrolysis in fluid-bed also requires further development and the yields of oil by this route could be optimized by hydrocarbonization under pressure. FT synthesis route is also considered to have limited applicability except perhaps in one or two large complexes where production of chemicals and fertilizers and pipeline gas could be integrated with produc-

tion of oil. The potential of liquid fuels and chemicals by both pyrolytic and FT routes is about 10 per cent by weight of coal as against 40-50 per cent of direct hydrogenation. The type of coal most suitable for direct hydrogenation is those from Assam, which have low ash, high sulphur, high convertibility to oil and large deposits. The nearness of these deposits to natural petroleum and gas also lends a special importance. The author suggests to combine the second stage (i.e. vapour phase) of coal hydrogenation, fluid-bed coking and production of chemicals and production and compression of hydrogen with a natural petroleum refinery.

For the proposed plant, the major products chosen are middle distillates, viz. HSD, kerosene and jet fuels; some naphtha will be produced (mainly from natural crude), which can be sold as premium gasoline or for chemical use (production of BTX, ethylene, propylene, butadiene, coke, ammonium sulphate, sulphur, etc.). Each unit, viz. coal-to-oil and natural crude refinery plants will contribute 30,000 bbl/day of total oil products. Naphtha may be considered for fertilizer production at site. The total plant investment is Rs. 220 crores, excluding costs of mining and power generation which together adding another Rs. 35.4 crores. About Rs. 113 crores of the total investment will be foreign exchange; however the import value of middle distillates is Rs. 35 crores/yr, excluding export potential of chemicals and saving of imports.

Of the total credits for sales for Rs. 980 million, approximately Rs. 600 is derived from chemicals and by-products. Allowing full capital charges and a built-in profit of 10 per cent on total plant investment to provide for loan repayment, the sale value for middle distillates ex-refinery is estimated at Rs. 166/ton compared to an average sale value of Rs. 180-200/ton at current market prices. The difference between sale value and production costs will enable a dividend to be paid at 6 per cent on equity capital even while full provision is made for loan repayment. In view of the potential of oil reserves of Assam coals (of the order of 500-750 m. tonnes and low proved reserves (100-155 m. tonnes) of natural petroleum, further study of the project from R&D and exploration as well as more techno-economic survey appear to be justified.

Coal, being cheap and abundant in India, can be competitive with other feedstocks for nitrogenous fertilizer industry⁵. Although overall capital investment is higher than in a naphtha based plant, the lower price of

⁴ Techno-economic Feasibility of Production of Oil from Upper Assam Coals.

⁵ Coal-Based Ammonia Plant by A. K. De and B. Chatterjee (see review under 'Technical Digests', p. 62).

coal nullifies the effect of fixed charges in the cost of production in a coal-based plant.

The paper⁶ by P. D. Sunavala (IIT, Bombay) discusses the possibilities of manufacturing methanol from coal via synthesis gas in the light of world shortage of crude oil and naphtha. The oxygen consumption per ton of methanol produced in the case of lignite appears less than half that of bituminous coal. This synthesis involves high pressures and the oxygen requirement is also heavy. Integration of methanol production with low or medium temperature carbonization of low rank coal is worth looking into—lignite pyrolysis gases almost yield a synthesis gas. The author suggests using large steam turbine-driven centrifugal compressors, which can be economic for handling large volume of gas. For small plants, there may be greater scope for using low pressure methanol synthesis by the ICI process. Since large amounts of carbon dioxide is produced in the gasification of coal a major outlet has to be found for carbon dioxide—say a dry ice or urea plant—as well as nitrogen from the tonnage oxygen plant. According to the author, nitrogen can be utilized for ammonia synthesis for which hydrogen can be prepared from steam-iron process. However, since the latter process requires carbon monoxide for reduction of iron ore following its oxidation with steam, another by-product, say blast furnace gas, has to be located for doing this. Thus, he concludes the methanol plant may be integrated with a steel plant where BF gas is available, which leads to two alternatives viz. integration with blast furnace operating on basic open hearth or LD process. In the case of basic open hearth for each ton of methanol there will be 9 tons of pig iron and about 11 tons of fertilizer.

The author examines the investment cost against capacity, which he has shown for the 500 tons/day plant—optimum capacity—at about a third of 100 tons/day plant. He estimates that it should be possible to produce methanol in India at Rs. 600 a ton on 500 tons/day scale employing centrifugal compressor by utilizing the by-products, viz. carbon dioxide and nitrogen, by coupling with integrated iron and steel plants and utilizing blast furnace gas for producing hydrogen for ammonia synthesis by the steam-iron process.

In their paper⁷ P. H. Pichler, H. Schulz and B. R. Rao

⁶ Techno-economic Aspects of Production of Methanol from Coal.

⁷ Present Status of Hydrocarbon Synthesis from Carbon Monoxide in Hydrogen and New Investigations on the Mechanism Using Tracer Technique and Radio Gas Chromatography. This paper was read by the last author (B.R.R.) at a later session.

of Karlsruhe (W. Germany) have given an excellent review on the basic research carried out by them and their co-workers. They traced the development of hydrocarbon synthesis including various catalysts culminating in the establishment of about 15 commercial plants in Germany and elsewhere in the thirties using cobalt catalyst. Later, iron was developed as a catalyst for medium pressure synthesis. A passing reference of the working of the Sasolburg plant has been mentioned.

For studying the complex mechanism of the reactions taking place during hydrocarbon synthesis, using C¹⁴-labelled compounds, radioactivity measurement with gas chromatography is now being used for determining the activity of a large number of individual components. The authors conclude the following: (i) The paraffins are the final products of synthesis and do not take part in secondary reactions, whereas α -olefins take part. (ii) The secondary reaction of hydrogenation of olefins is mainly responsible for the paraffins.

Session 2: In the first paper⁸, G. R. Hill and S. A. Qader (Univ. of Utah, USA) have evaluated the conversion of high volatile coals, occurring in large reserves in western USA, to liquid fuels by the alternative processes of pyrolysis, solvent extraction and hydrogenation and conclude that in all the three processes the conversion was found to have been accomplished by a sequential occurrence of first and second order reactions, the actual sequence depending upon the types of processing. Coal conversion was 35, 96 and 82 per cent by pyrolysis, solvent extraction and hydrogenation respectively. Conversion of coal is mainly a 2-stage process wherein coal is converted to crude oil and then the latter is converted to the finished products. The processing of the first stage product depends mainly upon its quality. The solvent extraction process yielded the maximum product but of a very inferior quality, while the hydrogenation gave good yields of liquid and gaseous products and the crude oil was of a good quality; there is scope for improving the yields of products. Considering various factors involved in the first and second stages of the process coal hydrogenation process is the most promising for adaptation on a large scale both with dry and coal-oil-slurry in ebulating bed reactors and the feasibility of the process has already been demonstrated.

The above investigations have demonstrated the feasibility of producing gasoline as the main product and diesel oil and high Btu gas as the principal by-products, best results being obtained at 515°C 2000 psi using 15 per cent stannous chloride as catalyst. The

⁸ Liquefaction of Utah Coals.

authors have given conceptual processing schemes of both stages indicating the most logical and feasible approach for the production of the above mentioned products and calculated material balance.

D. K. Mukherjee, J. K. Sama, P. B. Choudhury and A. Lahiri (CFRI) have studied⁹ hydrogenation in a rocking-type autoclave with S.S. liners with the object of developing inexpensive iron-based catalysts having activities matching tin and molybdenum catalysts. The catalytic activity of the iron oxide in combination with sulphur was observed to be greatly enhanced by precipitating the oxide on coal. Even at 100 atm cold pressure and 400°C, the conversion, yield and quality of product was found to be comparable to that of the molybdenum catalyst. Although the concentration of iron catalyst is higher, it is believed to be within practical and economic limits. The tar yield with this modified iron catalyst was nearly 11 per cent of the d.a.f. coal converted and was comparable with that obtained for the molybdenum catalyst.

The most stable form of iron in the presence of hydrogen and hydrogen sulphide is ferrous sulphide. The catalytic activity of iron increases with increasing S/Fe or H₂S/H₂ ratio. X-ray diffraction studies on the spent catalyst indicate that iron oxide in combination with sulphur attains a maximum catalytic activity within a range of ferrous sulphide composition corresponding to a general formula FeS_{1+x} where the value of x lies between 0.04 and 0.1.

In the next paper¹⁰, D. K. Mukherjee *et al* (CFRI) have reanalysed two sets of published data obtained by the U.S. Bureau of Mines on the hydrogenation of Rock springs coal and anthraxylon obtained from Pittsburg seam coal and infer that hydrogenation reactions cannot be represented by an elementary mechanism. It is pointed out that the data are better interpreted when the correction factor for benzene insolubles is not included. The negative values obtained in certain cases if this correction were to be taken into account would appear to indicate that the correction does not have adequate validity. The observed change in the order from a lower to a higher value, resulting in a decrease in rate as the reaction progresses, is interpreted to indicate an interally generated interference in the system due to some opposing reactions resulting in the formation of benzene insolubles or accumulation of structural components of coal that resist hydrogen-

ation. The overall hydrogenation reaction consists of not one, but a series of parallel and consecutive reactions like pyrolysis, depolymerization, hydrogenation, hydrogenolysis, dehydrogenation, condensation, etc. The overall kinetic behaviour is influenced by a group of such reactions and depending on the reaction conditions and concentration of the reactants, either one or a group of such reactions may become predominant and thus determine the end result.

R. W. Hiteshue, Walter Kawa and C.O. Hawk of the U.S. Bureau of Mines have studied¹¹ the hydrogenation of a high volatile bituminous coal in a small continuous pilot plant to explore the feasibility of producing a distillate oil at low pressures. They obtained a distillable oil at 2000 psi using iron (1-2 per cent) and molybdenum (0.1-0.5 per cent), temperature being limited to 465°C to avoid coking. Although the total conversion of coal was 90 per cent, the yield of oil (b.p. < 325°C) was about 56 per cent. The heavy oil that is produced is just sufficient for the paste production. The throughput was in the range of 9-22 lb/hr/cft of reaction volume. Successful hydrogenation at such low pressures has been attributed to the long residence times coupled with the use of a low-ash reactive coal. Although these long residence times result in a large reactor volume and thus increase the reactor cost, it has been pointed out that in an overall hydrogenation complex, the cost of the reactor constitutes only a minor item. To successfully hydrogenate the higher rank coals under these conditions would undoubtedly require high concentrations of more active catalysts.

D. K. Mukherjee, *et al* (CFRI) have hydrogenated¹² a typical Assam coal to assess the production of liquid fuels and chemicals as by-product and reported the influences of various operating variables. The consumption of hydrogen under varying conditions of pressure, temperature and time were studied as a function of conversion, and increase in reaction temperature was observed to be more important in determining hydrogen consumption than either pressure or time. For the range examined, a linear rise in conversion with time of reaction has been observed. They have presented carbon distribution data in the various products of hydrogenation and observe that 90 per cent of the sulphur in coal could be removed. The production of gaseous hydro-

¹¹ Low Pressure Hydrogenation of Coal in a Continuous Pilot Plant.

¹² Effect of Reaction Variables on Hydrogenation of Baragolai (Assam) Coal by D. K. Mukherjee, J. K. Sama, S. K. Mukherjee, P. B. Choudhury & A. Lahiri.

⁹ Hydrogenation of Coal with Iron Catalysts.

¹⁰ On the Kinetics of Coal Hydrogenation by D. K. Mukherjee, P. Samuel and A. Lahiri.

Technical Digests

Studies on Catalysts for Fertilizer Industry

As in many chemical processes, catalysts play a decisive role in most of the important chemical reactions used in the fertilizer industry¹, such as (i) combination of nitrogen and hydrogen under pressure to form ammonia, (ii) controlled oxidation of ammonia to form nitrogen oxides, (iii) oxidation of sulphur burner gases to form sulphur, (iv) controlled splitting of hydrocarbons to yield hydrogen and oxides of carbon, and (v) in many gas purification steps where objectionable constituents, such as hydrosulphide, organic sulphur compounds, carbon monoxide, oxygen, etc., are eliminated.

Since the establishment of the first commercial synthetic ammonia plant at Oppau in 1910, various catalysts from iron, chromium, bismuth, nickel, osmium, molybdenum, ruthenium, etc. have been studied and finally an iron catalyst having one or two promoters (amphoteric oxide with an alkali oxide) has found commercial acceptance. For the ammonia oxidation reactions, 3-5 layers of finely woven platinum gauze is used.

The first large-scale commercial development of the process for manufacturing hydrogen from hydrocarbon and steam, which is an endothermic reaction, was carried out by the Standard Oil Co. in 1930. The catalysts employed are, in general, nickel deposited on various types of refractory materials. In the processing of hydrocarbons for production of ammonia, a good portion of the hydrogen is split off and recovered but the carbon separates and forms carbon monoxide and dioxide. Carbon monoxide is a suitable source of hydrogen by reacting it with steam below 500°C in presence of a catalyst; the catalyst found suitable is iron oxide alone or mixed with chromium or sometimes aluminium and magnesium oxides.

Since the establishment of the fertilizer factory at Sindri, studies have been directed here towards development of indigenous know-how and facilities for catalyst production to help for maintaining the country's ferti-

lizer production without depending on foreign sources. The following are some of the catalysts developed in the P & D Division of FCI Ltd: (i) Low temperature CO-conversion catalyst for the production hydrogen and synthesis gas, (ii) CO-conversion catalyst for production of hydrogen and synthesis gas, (iii) steam-methane reformation catalyst, (iv) steam-naphtha reformation catalyst, (v) steam-oxygen methane reformation catalyst, (vi) methanation catalyst for removal of carbon monoxide and dioxide, (vii) zinc oxide catalyst for desulphurization.

Some of these catalysts are already under commercial use at Sindri and Namrup units of FCI and are also going to be used at Barauni fertilizer project. A few of these have also been supplied to private and public sector fertilizer plants and also exported to Europe.

Catalyst studies have generally involved trial and error runs that are guided by basic, thermodynamic considerations of the possible intermediates. Such runs will remain necessary until the kinetics and the thermodynamics of the catalyst system can be predicted.

Since the phenomenon is basically of electronic origin, the electrical conductivity and the electronic spin resonance spectra give the most direct insight into the behaviour of the catalyst. P. K. Ghosh, J. S. Tiwari,



Dr. P. K. Ghosh (P & D Div., FCI Ltd.) presenting his paper

¹ Role of Catalysts in Fertilizer Industry, paper presented by P & D Div., FCI Ltd. at the ECAFE Conference on the Development of Fertilizer Industry in Asia & Far East, held at Bombay, during Nov. 18 to Dec. 2, 1963.

S. C. Sinha, N. Roy and A. Sarkar² have applied these techniques to zinc oxide-copper oxide, a low temperature CO-conversion catalyst, for finding the nature of the active phase. The catalyst pellets, before reduction in the converter, are supposed to contain only zinc oxide a diamagnetic substance and cupric oxide which is anti-ferromagnetic at room temperature; hence no ESR signal is expected from the unreduced samples. In practice, a strong signal corresponding to about 6×10^{20} spins/g. was observed (Fig. 1), which was interpreted as originating from cupric ions diffused in the zinc oxide lattice. On reduction this signal had vanished and a broad signal was observed instead (Fig. 2), which was interpreted as arising from defects in the $\text{Cu}_2\text{O-Cu}$ system formed from the bulk CuO . The disappearance of the previous signal can signify either migration of cupric ions out of the zinc oxide lattice or their reduction to the diamagnetic cuprous state. The electrical conductivity is expected to increase in the former case and decrease for the latter. Conductivity measurements confirmed the latter possibility.

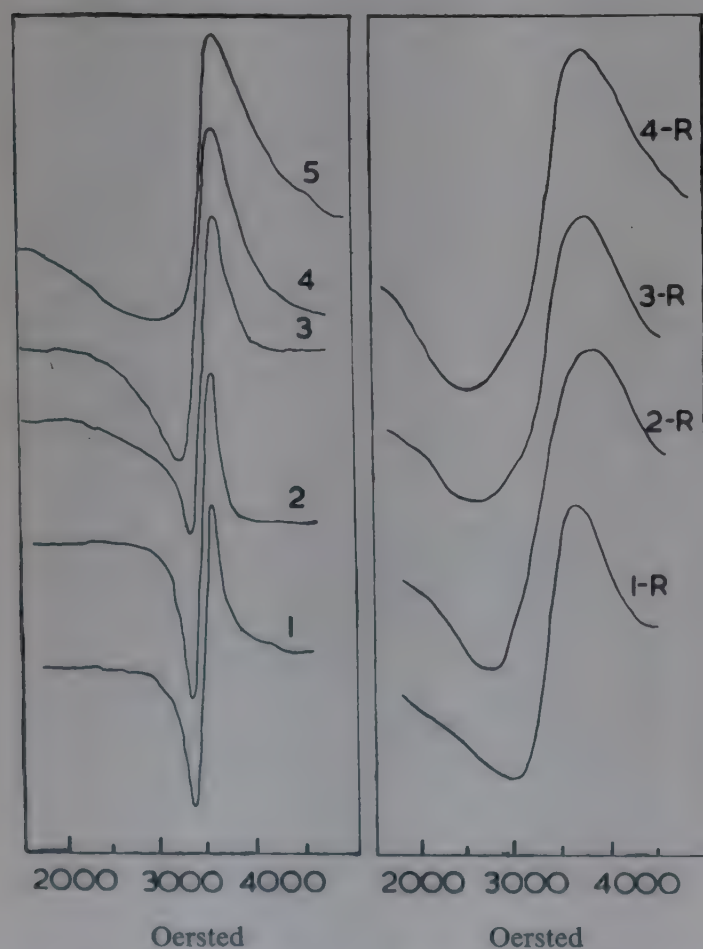


Fig. 1—ESR Spectra of Unreduced Catalysts

Fig. 2—ESR Spectra of the Catalysts after Reduction

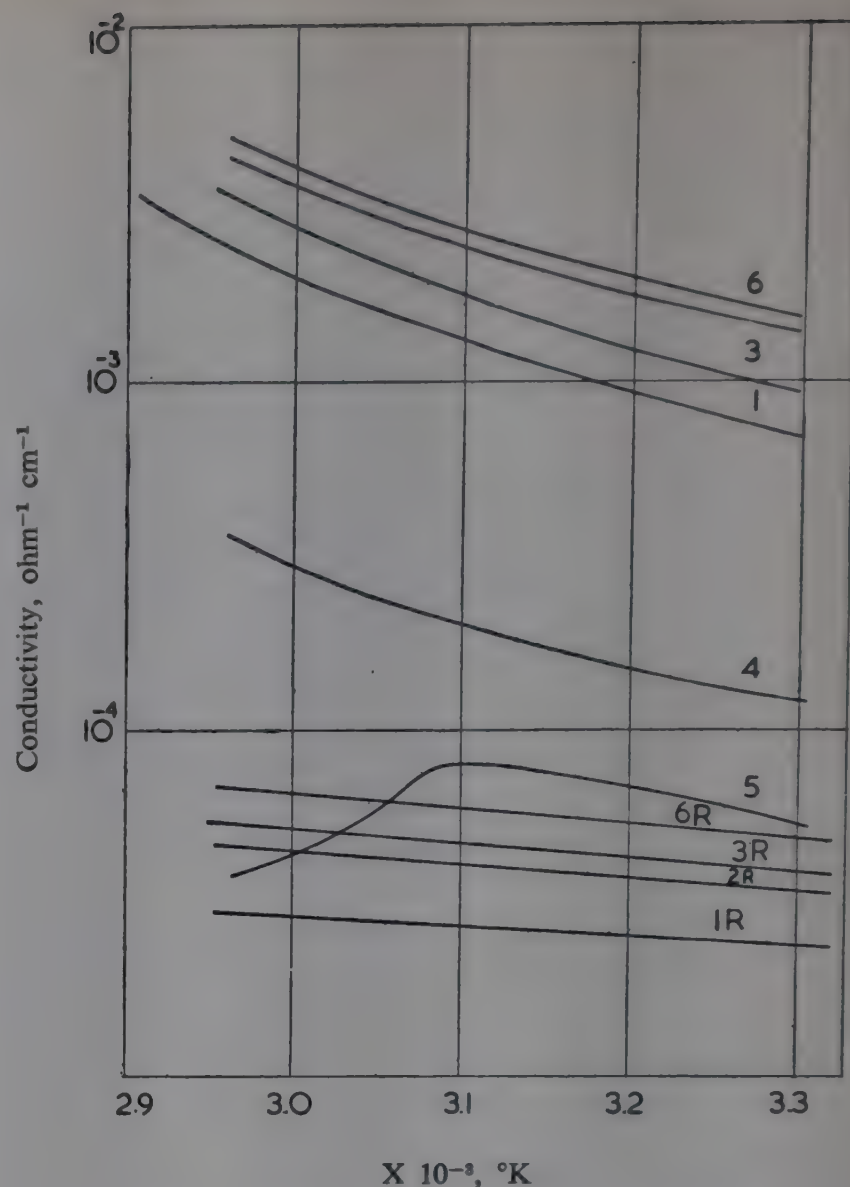


Fig. 3—Temperature Variation of Conductivity [The reduced samples are marked R]

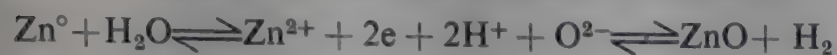
Moreover, from observations on the temperature variation of the electrical conductivity (Fig. 3), it was found that all the active catalysts were semi-conductors. A sample showing departure from this behaviour was inactive. Therefore, the previously held idea that metallic copper is the active phase is found open to doubt.

Zinc oxide, after the heat treatment during its preparation becomes oxygen-deficient and therefore contains a large number of donor Zn° centres. The cuprous ions constitute acceptor centres. Utilizing the common knowledge that neither zinc oxide nor copper oxide alone can catalyze the reaction, it is postulated that the presence of both donor and acceptor centres is necessary. The further necessity of physical nearness of the two types of centres is satisfied by the diffused cuprous ion model proposed here.

The authors have suggested the following probable reaction: Following the work of Cotton and Fensham [*J. Phys. Chem.*, 68 (1964), 1052], it is proposed that the cuprous ion sites acquire one chemisorbed atom of

² The Nature of the Active Component in Copper Oxide-Zinc Oxide CO-Conversion Catalyst, paper presented at the CFRI Symposium on Chemicals & Oil from Coal.

oxygen each obtained by the release of oxygen from the zinc oxide lattice. One molecule of carbon monoxide is chemisorbed on each such site to produce carbon dioxide which is then desorbed. The oxygen deficiency, thus created in the zinc oxide structure, is made up by the decomposition of water by the donor Zn° sites as



Zinc oxide, thus formed, may subsequently break down again to supply oxygen to the cuprous sites, thus maintaining the cycle.

The next paper³ by V. K. Puri, N. C. Ganguli and S. P. Sen, presented at the symposium, dealt with changes taking place in a catalyst during thermal treatment required to impart mechanical strength to it.

Physical structure and texture play an important role in determining the activity and stability of a catalyst. The authors have studied the changes effected in the physico-chemical properties of Fe_2O_3 and $\text{Fe}_2\text{O}_3\text{—Cr}_2\text{O}_3$ shift conversion catalysts when heated to elevated temperatures. These manifest themselves in decrease of the specific surface area, growth of the elementary particle and elimination of finer pores.

In shift converters, the working temperature is between 360 and 500°C with occasional overheating. In the present study, the probable temperature ranges from the 450 to 900°C have been scanned to ascertain the effect of temperature on structural parameters affecting activity. As a result of heat treatment, the catalytic activity decreases with the degree of sintering but this is less pronounced when chromium oxide is present in the system. Incorporation of chromium-oxide helps the catalyst in retaining its surface area and activity to a much greater degree than the corresponding values without having chromium. At 900°C, the surface area invariably tends to attain a limiting value in both the cases. A linear relationship exists between conversion efficiency and surface area of the reduced ferric oxide and $\text{Fe}_2\text{O}_3\text{—Cr}_2\text{O}_3$ type catalysts (Fig. 4).

During the reduction of Fe_2O_3 , the surface area decreases and the pore volume of the catalyst increases. The data on Cr_2O_3 addition amply demonstrate that it inhibits these changes to a considerable extent and at the same time enhances the activity. Although ferric oxide has a highly developed surface, yet when it is reduced to ferroso-ferric oxide (Fe_3O_4) the loss in surface area is considerable and average grain size also increases. When

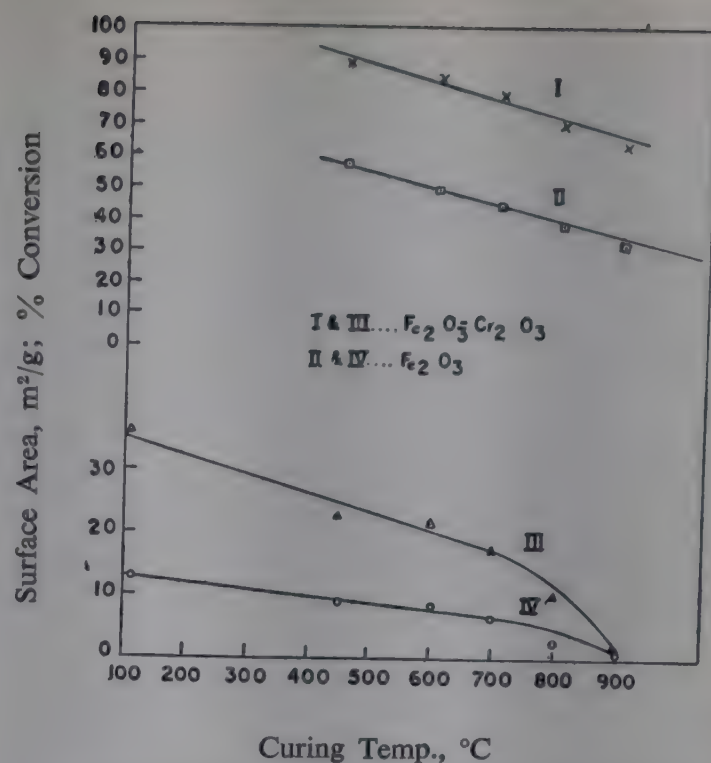


Fig. 4—Specific Surface Area and Conversion of Reduced Sample against Curing Temperature

ferric oxide samples are cured from 110 to 900°C the number of bigger pores increases in the range $r = 500\text{--}75000 \text{ \AA}$ and this phenomenon has been observed both before and after reduction and shows that samples in which the surface area is large, the number of finer pores is large as compared to samples where the surface area is small.

By incorporating chromium oxide in ferric oxide the tendency to increase the grain size and shrinkage in surface area is arrested and the mechanical strength is not retained but tends to increase after reduction.

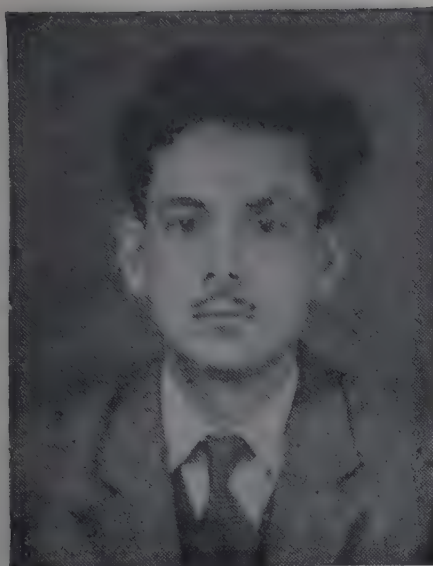
The phenomenon of growth of larger particles and elimination of finger pores may be attributed to sintering. With increase in temperature the pores upto 400 Å tend to disappear.

With increase in the temperature of curing from 450 to 600°C, there is some increase in mechanical strength but beyond this temperature the degree of changes leading to decrease in surface area and activity is high.

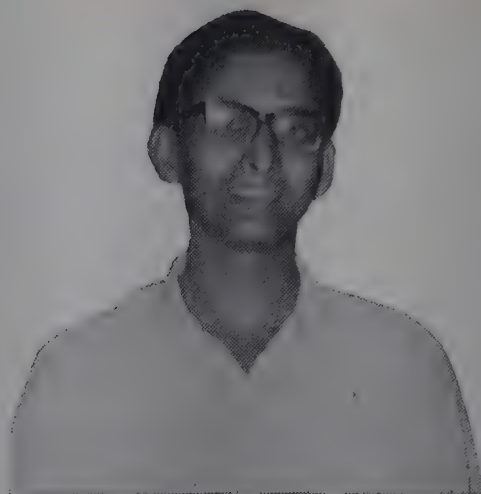
The results presented provide guidance for the assessment of the changes in the structural parameter and associated activity. Under identical methods of preparation and heat treatment, there exists linear relationship between the surface area and conversion efficiency on one hand and curing temperature and conversion efficiency on the other.

Alumina-nickel and alumina-silica-nickel catalysts are used in many industrial catalytic processes. In the fertilizer industry such catalysts are widely used in the refor-

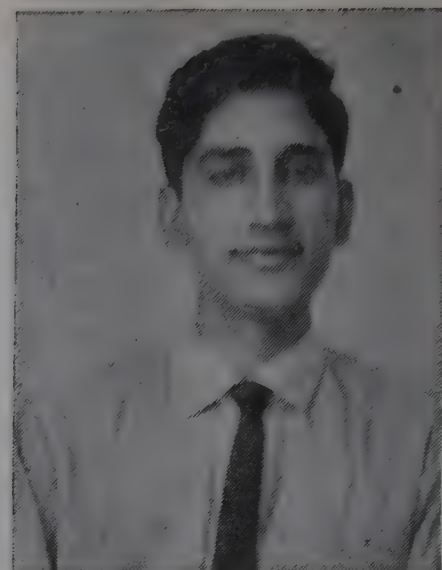
³ The Effect of Thermal Treatment on the Physico-chemical Parameters of Fe_2O_3 and $\text{Fe}_2\text{O}_3\text{—Cr}_2\text{O}_3$ Type Shift Conversion Catalysts.



N. C. Ganguli



B. Sen



B. R. Arora

Some of the other scientific workers of P & D Division, who read papers at the CFRI Symposium are: Sarbasri N. C. Ganguli, B. Sen and B. R. Arora.

mation of hydrocarbons, for which several types are commercially available. Such catalysts, however, show a wide variation with respect to their nickel content (2.5 to 30 per cent), activity, oxidation-reduction characteristics, etc. The reduction operation of the reformation catalyst is a vital step before allowing for the specific reaction to take place and all catalyst manufacturers stipulate the reduction procedure to be followed for a particular type of catalyst. B. R. Arora, R. K. Banerjee, N. C. Ganguli and S. P. Sen have studied⁴ the reduction of nickel oxide in a commercial type reformation catalyst by a thermogravimetric method, keeping in view how the method of preparation and nickel concentration can influence the rate and extent of reduction.

It has been observed that the rate and extent of reduction depend upon the mode of incorporation and concentration of nickel in the catalyst. Hill and Selwood [*J. Amer. Chem. Soc.*, 71 (1949), 2522] are of opinion that the first increment of nickel impregnated on the support interact strongly and selectively. With increasing nickel concentration, the sites become saturated and deposit either over occupied sites or in close proximity, and act as a bulk nickel oxide, hence are easily reducible. At lower concentration, nickel has a higher oxidation state than two. Alumina exerts an inductive action on the nickel leading it to assume a radius and oxidation state which fits in its lattice. With increasing concentration this structure gets distorted.

The findings of steam oxidation indicate that the extent

to which reduced nickel can be oxidized is related to the reducibility of a catalyst; in general, the catalysts in which the extent of reduction is more, the extent of oxidation of the reduced nickel is correspondingly higher.

An increase in surface area of the sample having the lowest nickel concentration was observed compared to alumina support alone. This increase can be explained by assuming the additive mixing of alumina particles with nickel particles of the same shape. These samples have smaller crystallite size and are reduced with difficulty. A relative decrease in the surface area with the increase in nickel concentration can be explained only by assuming that alumina surface decreases during successive impregnation in which all the pores and cavities are filled up by the same nickel particles. This causes an increase in the crystallite size and such samples are easy to reduce. The relative decrease in surface area is altogether absent in the precipitated samples, which again confirms that in these samples distribution of nickel is different and the metal is very finely dispersed in the catalyst to offer resistance to reduction. The crystallite size also is in the same range and does not increase with increasing nickel concentration.

A radically new concept of the mechanism of catalysis has been provided by S. P. Sen, B. Sen and D. K. Mukherjee in their paper⁵. It is based on Chakravorty's theory of the Universal Spherical Wave of Energy Field and Atom [*Technol.*, 1(1964), 3 Spl. Issue], according to which right from the universe up to the atom,

⁴ Thermogravimetric Investigations on Reduction and Oxidation Properties of Reformation Catalyst, paper presented at the CFRI Symposium on Chemicals and Oil from Coal.

⁵ New Concept in the Field of Catalysis based on Universal Spherical Wave Theory, paper presented at the CFRI Symposium.

the associated processes of their formation and manifestations are different stages of a continuum. The present paper⁵ is the application of Chakravorty's generalized concept of universal spherical wave of energy-matter-space-time equilibrium to the mechanism of catalysis. After giving an outline of the theory of universal spherical wave, the authors have explained the concepts of gas, liquid and solid in the light of this theory. According to it, the catalyst must have a configuration with fundamental and derived dimensions. Equilibrium catalyst configuration may be conceived as tetrahedral in nature with fixed centroid vibrating between two phases, where all derived positions are not occupied.

The authors also compared this concept with the existing theories and show that it explains the general aspects of catalysis; it is not a contradiction to any of the existing theories; on the other hand, the model presented gives a clearer picture of the catalytic processes. To examine the relative merits of this concept, the well-known ensemble theory of Kobozev [*Zhav Fiz Khim*, **31** (1957), 2162] has been taken into consideration and discussed in detail. It has been shown that the new concept compares very well with that of Kobozev's model.

Alternate Feedstock and Corresponding Design Features of Ammonia Plant

In India, in choosing feedstock and processes to meet our increasing ammonia requirement, one has to take into account the availability position of feedstock. Since our requirements of fertilizer are massive and that we cannot afford to commit ourselves to recurring expenses in foreign exchange to fill in our needs by sustaining imports of finished goods or preferred raw materials for processing. The present day shift of emphasis away from use of lighter feedstock like naphtha to less favoured ones, like heavier refinery stock, coal etc., has to be viewed in this context. This observation was made and elaborated by Dr. K. R. Chakravorty at 'National Seminar on Fertilizer Production and Technology' held at New Delhi under the auspices of Fertilizer Association of India*.

In the manufacture of ammonia source of nitrogen is invariably atmospheric air. But hydrogen is to be obtained either from water or hydrocarbon feedstock by a suitable sequence of chemical reactions. Winning hydrogen from water by electrolysis is highly power-intensive operation and can be economically competitive only where large blocks of power are available at very low costs. This source is preferred where fossil fuel falls

short in supply or may prove costly due to remoteness of source. In hydrocarbon feedstocks, the hydrocarbon constituents vary in complexity from a lighter feedstock to heavier liquid and solid feedstock; while natural gas or light straight distillates from crude contain comparatively pure and simpler hydrocarbons and the heavier stock represents more complex combination of hydrocarbon, richer in carbon than in hydrogen and often associated with inert ash which complicates processing steps. The primary step in processing hydrocarbon feedstock is to split up the hydrocarbons to liberate hydrogen and isolate carbon as oxides which may be brought about by reaction with oxygen and/or steam. The feedstock should have some characteristics. These are: it should be capable of being handled as vapour at processing condition and free from sulphur, and should predominantly consist of saturated hydrocarbons, preferably straight chain, unsaturates are to be limited to 1.5 per cent by weight and aromatics to about 20 per cent. To meet these characteristics, maintained the author, in practice, feedstock is generally catalytically hydrogenated converting all unsaturates to saturated compound and sulphur to hydrogen sulphide which can be easily removed. But in the heavier feedstock, oxygen is used to split the hydrocarbons at high pressure without using any catalysts and this operation is essentially an autothermal one. While high pressure partial oxidation has been applied successfully to all heavy liquid feedstock, no commercial unit has yet been tried out for processing solid fossil fuel, even fed as slurries. The removal of ash from pressure chamber poses technological problems, yet to be successfully solved.

The principal processing steps for conversion of raw synthesis gas to ammonia synthesis mixture covers the following operations which in the opinion of the speaker may or may not be adopted in their sequence: (i) Removal of sulphur and other harmful constituents from the gas; (ii) realisation of full potential hydrogen from raw gas by carrying out a water gas shift reaction of carbon monoxide with steam to segregate carbon predominantly as carbon dioxide and generate equivalent hydrogen from steam; (iii) bulk removal of carbon dioxide from gas; (iv) finishing operations to reduce carbon dioxide residuals in gas to less than 5 ppm.

Then Dr. Chakravorty described the salient features of the various steps involved in the above process sequence. The recent advances in various branches of technology and application of new alloys are finding place in modern gas or naphtha-based ammonia plant. This has resulted in increasing pressure of operation higher and corresponding decrease in equipment size. Apart from bring-

* on Dec. 14-16, 1969

ing in a saving on per unit investment cost of ammonia plants, this has brought in trend for close integration of the total energy system of the assembly to provide for maximum recovery and re-use of by-product energy from process stream requirements within the plant. Processes which can be carried out principally in static catalyst beds gain a preference in design and a suitable catalyst of increased activity as well as specificity have also been developed and applied increasingly in the new flow schemes. Typical process sequences incorporating these various improvements in techniques were illustrated by the author.

The speaker pointed out that when proceeding from lighter feedstock to heavier solid fossil fuels, the hydrocarbons forming the basic starting materials assume higher and higher molecular weights and structural complexity. The carbon-to-hydrogen ratio in the feedstock increases. As a logical sequence raw gases obtained tend to be richer in carbon oxides. Duties on water shift conversion, carbon dioxide removal and other sections progressively increase. Steam requirements go up. Catalyst volumes, equipment size and ratings, etc. also tend to get enlarged. The plants for heavier feedstock thus tend to acquire bigger sizes (often requiring multiple units) and call for increased investment. Based on 900 tonnes/day naphtha-based ammonia plant and investment index taken 100, fuel oil and coal-based plant in-

vestment index would be 116.5 and 128 respectively. There is, however, some compensation on operation costs due to the fact that price of fuel equated in terms of Kcals is much higher in case of lighter feedstocks than the grosser and heavier fuels. The total energy requirements for intergrated and energy intensive ammonia plants as per modern trends based on various feedstocks given below, felt the author, should be studied to understand why less favoured feedstocks, like heavier refinery oil, coal, etc., are being sought after. (Table 1)

Coal-Based Ammonia Plant

With the recent development in process of hydrocarbon-steam reformation at high pressure and adoption of single stream large size units with an intergrated system for driving main compressors, pumps, etc., the economy of fertilizer industry has reached a new stage. There is now a tendency to concentrate on large scale ammonia plants based on natural gas and naphtha. However, our resources of natural gas and naphtha are limited. By 1973 the total annual production of motor spirit naphtha from all refineries is expected to be 4.177 million tonnes, out of which 2.496 m.tonnes would be released for fertilizer and petrochemical industries. Naphtha already slated for the above industries is 2.955 m.tonnes, meaning a deficit of 0.459 m.tonnes.

In a paper presented at the symposium on Chemicals

TABLE 1—AMMONIA PRODUCTION WITH DIFFERENT FEEDSTOCKS*

Sl. No.	Item	Ammonia from Naphtha Refor-mation	Ammonia from Oil	Ammonia from Coal Gasification
1.	Energy with feedstock, Kcal per tonne	8.55×10^6	7.82×10^6	9.83×10^6
2.	Energy supplied by service Boiler Kcal per tonne	0.07×10^6	4.313×10^6	4.85×10^6
3.	Energy Recovered from Carbon pellet Kcal per tonne	—	0.104×10^6	—
4.	Net energy supplied Kcal per tonne	8.62×10^6	12.029×10^6	14.68×10^6
5.	Electric power required kWh per tonne	289	554	775
	Equivalent Kcal per tonne in fuel	0.83×10^6	1.59×10^6	2.22×10^6
6.	Total energy Kcal per tonne	9.45×10^6	13.619×10^6	16.90×10^6
7.	Cost of feedstock (Rs.)	112.50	100.00	54.60
8.	Cost of fuel for steam and power generation (Rs.)	4.98	32.70	39.20
9.	Credit for carbon pellets (Rs.)	—	(-4.68)	—
10.	Total cost of Raw Material (Feedstock-fuel) (Rs.)	117.48	128.02	93.80

* based on following assumed costs.

Naphtha	—	Rs. 138.08/tonne and cost per 10^6 Kcal 13.15
LSHS	—	Rs. 131.71/tonne and cost per 10^6 Kcal 12.80
Coal	—	Rs. 36.00/tonne and cost per 10^6 Kcal 5.54
Carbon pellets	—	Rs. 350.00/tonne and cost per 10^6 Kcal 45.00

and Oil from Coal held at Central Fuel Research Institute during Dec. 6-8, 1969, Sarbasri A. K. Dey and B. Chatterjee suggested for coal-based ammonia plants. There are vast reserves of non-coking coal in our country and in many locations although facilities have already been developed for large-scale mining, such coals are not being utilized for lack of demand. Therefore, large scale coal-based fertilizer plants can be located in such areas which will have significance in the overall national economy. In this context, the authors cited several coal-based plants running competitively in some European countries where coal is available at a cheaper rate. In Turkey a new ammonia plant has been put into commission using locally mined lignite. Similarly in Spain also, an ammonia plant with locally mined lignite as feedstock is running for the last 10 years without any suggestion for abandoning it.

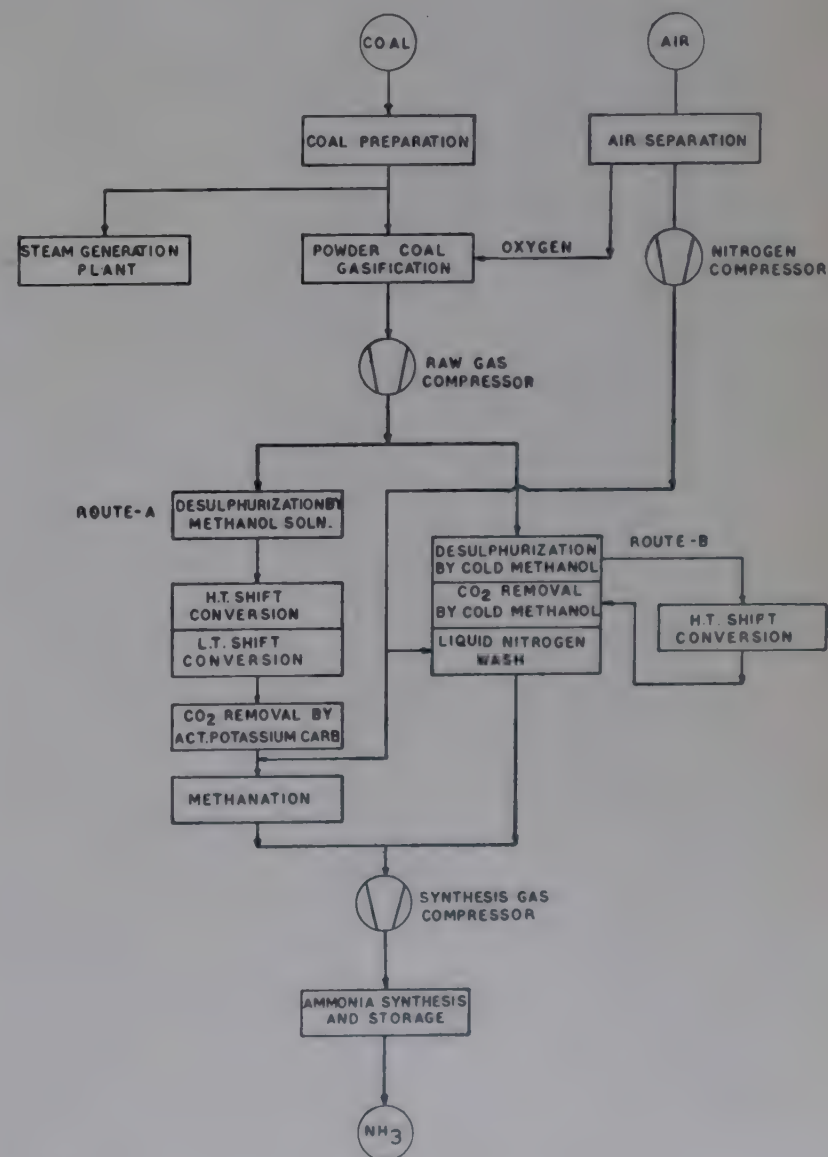
The production of ammonia from coal involves the following steps: (1) gasification of coal and production of raw gas principally comprising hydrogen and carbon monoxide; (2) processing of raw gas and its purification with correct proportion of hydrogen and nitrogen for ammonia synthesis and (3) final compression and ammonia synthesis.

Of the available processes, gasification of coal as a fine dust in suspension with a co-current flow of oxygen at low pressure is particularly suitable for producing ammonia synthesis raw gas. It gives in a single step a raw gas rich in carbon monoxide and hydrogen and inert residuals (argon and methane) limited to less than 1 per cent, a composition eminently suitable for processing in a conventional gas purification train using commercially proved processes. It can be charged with wide varieties of coal with varying caking characteristics, ash contents and ash melting points. The process involves a feed preparation section, where coal is finely powdered and also dried simultaneously to a low moisture content in a closed circuit system using ball mills. The coal preparation section may be designed in two streams with capacity of handling coal required for 1000 te/day ammonia production. Three gasifiers will be able to handle coal dust producing the raw gas. Ash from the gasifier is removed in a molten stage, quenched into granules and scraped away for disposal. Raw gas at high temperature is passed through a heat recovery system, thereby raising high pressure steam, and is then taken through a series of gas cleaning arrangements. The lean gas is then compressed in a single stream turbine-driven centrifugal compressor handling gas equivalent to 1000 te/day ammonia to a pressure of 30-35 kg/cm².

A single stream air separation plant can meet all the

demand of oxygen in the gasification section and also the nitrogen requirement for synthesis gas mixture.

Processing and Purification of Raw Gas: The raw gas is desulphurized by circulating a methanol solution at a comparatively higher temperature in a tower to less than 0.2 ppm sulphur. The gas then flowing through a series of heat exchanges enters the shift conversion tower packed with high temperature shift catalyst in a multi-layer bed, where carbon monoxide is reduced to 3 per cent adding up an equivalent quantity of hydrogen in the converted gas. It then flows into the second tower at a lower temperature packed with low temperature shift conversion catalyst where carbon monoxide is reduced to 0.3 per cent. To safeguard the 1. t. catalyst against sulphur poisoning a catalyst bed of zinc oxide precedes the 1.t. catalyst. The converted gas is then led to the decarbonation section, where carbon dioxide is scrubbed with a stream of activated potassium carbonate solution



Typical Flow Scheme for a Large Capacity Coal-Based Ammonia Plant

thus reducing, it to 0.1 per cent. The final purification is accomplished by a catalytically converting carbon monoxide and dioxide still present in the gas stream in a catalyst packed tower. A correct proportion of nitrogen is added to the stream before it flows to the methanator. The methanated gas is finally compressed and sent to ammonia synthesis section. (See Flow Diagram on p. 63.).

The coal-based plants in India have a definite signi-

ficance, considering strategy, national economy and lower price of coal. Though the overall capital investment is higher than in the similar capacity plant, the lower price of coal will nullify the effect of mixed charges in the cost of production of ammonia. Also, the cost of power, which contributes appreciably in the cost of production of ammonia in a coal-based plant is minimized to about 450 kW/te of ammonia by adopting the new technology.

measurements were made by a Kaycee potentiometer using a low impedance Pye scalamp galvanometer. A minimum of two readings was taken in each case. In most cases, steady state was reached in 6 hr. but at times it took even 18 hr. Both anodic and cathodic polarization data were taken and an interval of 3 min. was allowed between each reading after the start of the polarizing current.

Results and Discussion

The weight-loss data obtained earlier and the open circuit potential values of coupons are recorded in Table 1. More or less the same potential values were obtained with or without the inhibitors except in presence of sodium nitrite where cathodic shift in potential was observed. The combination of sodium nitrite with other inhibitors also produced a cathodic shift and the most noble potential was obtained with a mixture of sodium nitrite and the soluble oil.

TABLE 1—OPEN CIRCUIT POTENTIAL AND WEIGHT-LOSS DATA WITH MILD STEEL IN DEGASIFICATION SECTION WATER

Nos.	Inhibitors	Open Circuit Potential Vs S.C.E., mV.	Weight- Loss, mg./sq. dm/day.
1.	None	- 716	90.5
2.	Sodium Nitrite (4 g./l)	+ 28	—
3.	Sodium Benzoate (4 g./l)	- 704	109.8
*4.	Soluble Oil (2 ml./l.)	- 694	65.0
5.	Ammonium Thiocyanate (1 g./l)	- 693	165.2
6.	Sodium Nitrite (4 g./l.) + Soluble Oil (2 ml./l)	+ 120	18.0
7.	Sodium Nitrite (4 g./l.) + Sodium Benzoate (4 g./l)	+ 45	—
8.	Sodium Nitrite (2 g./l) + Ammo- nium Thiocyanate (1 g./l) + Solu- ble Oil (2 ml./l)	+ 67	10.7
9.	Sodium Nitrite (4 g./l) + Sodium Benzoate (4 g./l) + Soluble Oil (2 ml./l.)	+ 110	—
10.	Sodium Nitrite (2 g./l.)	—	320.7
11.	Sodium Nitrite (2 g./l) + Sodium Benzoate (4 g./l.)	—	589.5
12.	Sodium Nitrite (2 g./l.) + Ammo- nium Thiocyanate (2 g./l.) + Solu- ble Oil (2 ml./l.)	—	14.9
13.	Sodium Nitrite (2 g./l.) + Sodium Benzoate (4 g./l.) + Soluble Oil (2 ml./l.)	—	9.6

* Gulf-Sil Soluble Oil.

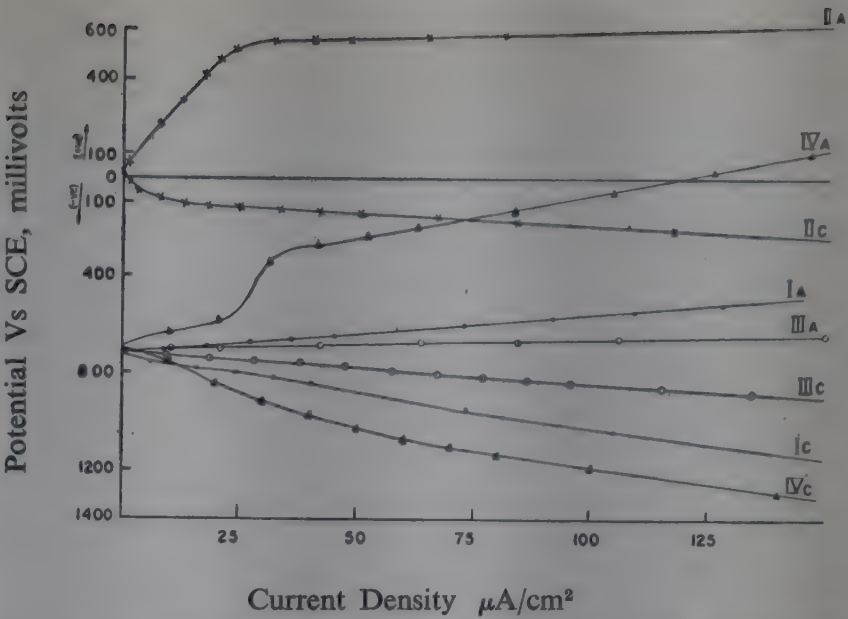


Fig. 1—Polarization of Mild Steel in Presence of Single Inhibitors
Anodic
IA—Without Chemical Inhibitor ; IIA—With 4 g/l Sodium Nitrite ; IIIA—With 4 g/l Sodium Benzoate ; IVA—With 2 ml/l Soluble Oil
Cathodic
IC—Without Chemical Inhibitor ; IIC—With 4 g/l Sodium Nitrite ; IIIC—With 4 g/l Sodium Benzoate ; IVC—With 2 ml/l Soluble Oil

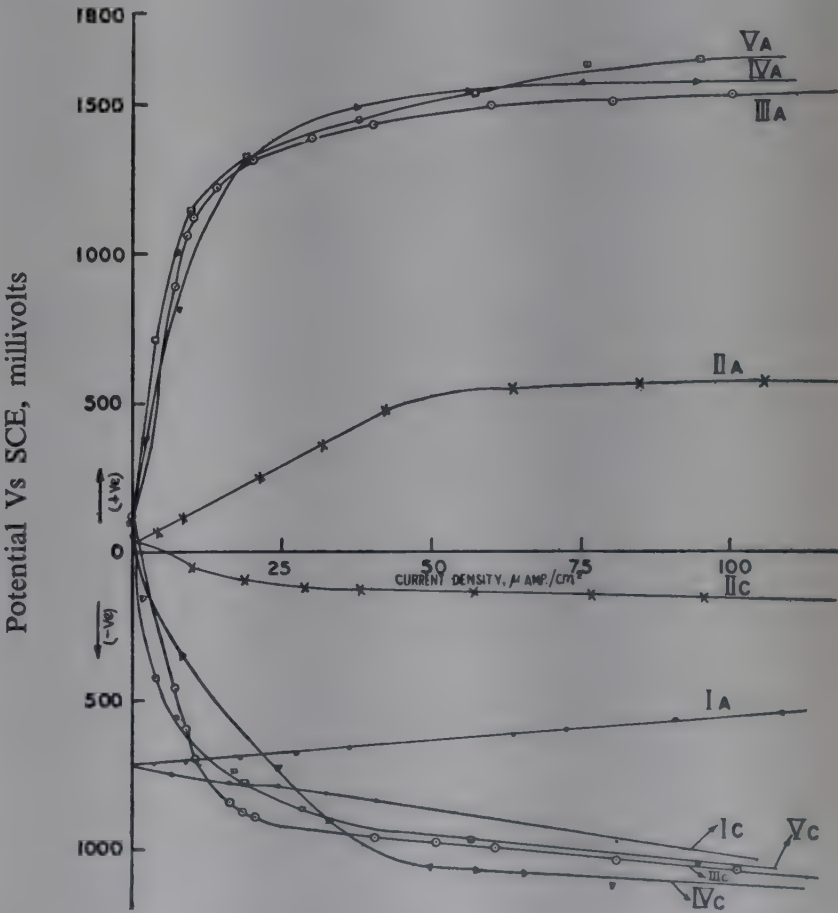


Fig. 2—Polarization of Mild Steel in Presence of Mixed Inhibitors
Anodic
IA—Without Inhibitor ; IIA—With 4 g/l Sodium Nitrite+4 g/l Sodium Benzoate ; IIIA—With 4 g/l Sodium Nitrite+2ml/1. C Oil ; IVA—2 g/l Sodium Nitrite+1 g/l Ammonium Thiocyanate + 2 ml/1 Soluble Oil ; VA—4 g/l Sodium Benzoate+4 g/l Sodium Nitrite+2ml/1 Soluble Oil
Cathodic
IC—Without Inhibitor ; IIC—With 4 g/l Sodium Nitrite+4 g/l Sodium Benzoate ; IIIC—With 4 g/l Sodium Nitrite+2 ml/1 Soluble Oil ; IVC—2 g/l Sodium Nitrite+1 g/l Ammonium Thiocyanate + 2 ml/1 Soluble Oil ; VC—4 g/l Sodium Benzoate+4 g/l Sodium Nitrite+2 ml/1 Soluble Oil

The extent of polarization has been shown in Fig. 1. All the curves except that corresponding to sodium nitrite follow a straight line course. The mild steel electrode without inhibition was more polarized cathodically than anodically; thus, the corrosive attack was under cathode control. The increased anodic polarization due to the soluble oil indicated its greater inhibitive properties. Sodium nitrite indicated substantial polarization while with sodium benzoate it was negligible.

Polarization curves for combination of inhibitors have been shown in Fig. 2. Combination of sodium nitrite and sodium benzoate showed more anodic polarization than cathodic but the extent of polarization was small. Curves II, III and IV show considerable cathodic and anodic polarization even at very low current densities; at current

densities higher than $25 \mu \text{A}/\text{cm}^2$ the extent of polarization became nearly constant as indicated by the near horizontal curves. In all the three cases, the anodic polarization was much more pronounced than the cathodic one. These three combinations—viz. sodium nitrite + sodium benzoate, sodium nitrite + soluble oil and sodium nitrite + ammonium thiocyanate + soluble oil—have been shown to be good inhibitors by weight-loss data as well¹. Thus, in the present case a correlation is shown between polarization and weight-loss data of mild steel in a corrosive environment in presence of inhibitors.

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Various intermediates and their amounts formed by different processes in the manufacture of nitrophosphates have been studied by X-ray diffraction method, using sodium fluoride as an internal standard.

Double Salts and Solid Solutions in Nitrophosphates

By V. K. SRINIVASA AND S. K. GHOSH,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

In the manufacture of different grades of nitrophosphates with or without potassium from the usual components by different conventional processes, many double salts and solid solutions can form by reaction between the initial and final products, besides the usual chemical reaction. It is difficult to characterize these intermediate compounds formed and their proportions by chemical analysis alone. The accuracy probably is best determined by comparison of the chemical composition computed from x-ray analysis with that obtained by chemical analysis. The information regarding the various intermediates and their amounts formed by different processes

in the manufacture of nitrophosphate is important from the point of view of process control. In view of this, various commercial nitrophosphates produced by different processes by the leading manufacturers of the world have been examined by x-ray diffraction method.

Experimental

The x-ray diffraction patterns of different grades of nitrophosphates were obtained with nickel filtered $\text{CuK}\alpha$ radiation, the x-ray tube running at 40 kV and 20 mA. The phase identification was done by the usual method of Hanawalt *et al*¹. Ando *et al*² adopted the quantitative

x-ray diffraction method of analysis to fertilizers using spinel (MgAl_2O_4) as an internal standard. The same procedure has been adopted in the present study using sodium fluoride which does not react with the common fertilizer components as an internal standard. The diffraction peaks of sodium fluoride is free of interference from those of many compounds.

The calibration curves were made for common fertilizer salts, several double salts and solid solutions, often present in nitrophosphates. Pure ingredients were used for this purpose. The presence of amorphous materials and the compounds less than 2 per cent could not be detected by x-ray examination.

Discussion

The major commercial nitrophosphate processes and their principal components are listed in the Table 1.

The chemical analysis of the final products, whose exact formulations are not known, are given in Table 2.

The compounds in the potash-free granular fertilizers are mainly ammonium nitrate, ammonium phosphate, dicalcium phosphate, and gypsum; in some products, components like ammonium sulphate are also detectable. Apatite is present in most of the products and its amount varies from 2 to 7 per cent by weight. All the nitrate is present as ammonium nitrate (IV), except in some cases where the amount of ammonium sulphate being high, a part of it is present as $\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$; it has either reacted with ammonium nitrate to form the double salt $\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ or with CaSO_4 to form syngenite. The amount of syngenite formed is very small.

The compounds present in the granular nitrophosphates after addition of potash are very complex; most of the potassium chloride has reacted with ammonium

TABLE 1—PRINCIPAL COMPONENTS AND CRYSTALLINE PHASES IN NITROPHOSPHATES PREPARED BY DIFFERENT PROCESSES

Process	Principal Components in the Product	Grades N-P ₂ O ₅ -K ₂ O	Minor Phases	Other than Principal Components Present	
				Double salt (DS)/Solid solutions (SS)	
				System	Percentage
Carbonitric	NH ₄ NO ₃ CaHPO ₄ CaCO ₃	16-13-0	NH ₄ H ₂ PO ₄ MgSO ₄ , Apatite	—	—
Sulphonitric	NH ₄ NO ₃ CaSO ₄	13-13-0	MgSO ₄ , CaF ₂ , Quartz	2NH ₄ NO ₃ (NH ₄) ₂ SO ₄ (DS)	4
Sulphonitric	CaHPO ₄	20-20-0	Apatite, CaF ₂ Ca(NO ₃) ₂ 4H ₂ O	CaSO ₄ (NH ₄) ₂ SO ₄ H ₂ O (DS)	3
Unknown	NH ₄ H ₂ PO ₄ (NH ₄) ₂ HPO ₄ (NH ₄) ₂ SO ₄	20-18-0	Apatite, α-Fe ₂ O ₃ α-Al ₂ O ₃ Quartz.	NH ₄ (NO ₃) (NH ₄) ₂ SO ₄ (DS) 3NH ₄ NO ₃ (NH ₄) ₂ SO ₄ (DS)	3 5
		23-23-0	Apatite	—	—
Odda	NH ₄ NO ₃	24-16-0	CaSO ₄ (NH ₄) ₂ SO ₄	CaSO ₄ (NH ₄) ₂ SO ₄ H ₂ O (DS)	3
Kampka	NH ₄ H ₂ PO ₄ (NH ₄) ₂ HPO ₄	26-17-0	CaF ₂	2NH ₄ NO ₃ (NH ₄) ₂ SO ₄ (DS)	4
Sulphate Recycle	CaHPO ₄				
Mixed Fertilizer	NH ₄ H ₂ PO ₄ , Ca(H ₂ PO ₄) ₂ H ₂ O NH ₄ cl, CaSO ₄ 2H ₂ O	10-10-10	(NH ₄) ₂ SO ₄ , KCl.	K ₂ SO ₄ CaSO ₄ H ₂ O (DS)	18
		—	—	(7:3) (NH ₄) ₂ SO ₄ -K ₂ SO ₄ (SS)	6
	(NH ₄) ₂ HPO ₄ , CaSO ₄ 2H ₂ O NH ₄ Cl, K ₂ SO ₄ , Kcl	10-20-20	(NH ₄) ₂ SO ₄	(2:8) NH ₄ Cl-Kcl. (SS)	5
		—	—	(9:1) NH ₄ H ₂ PO ₄ -KH ₂ PO ₄ (SS)	4
		—	—	K ₂ SO ₄ CaSO ₄ H ₂ O (DS)	12
	KCl. NH ₄ Cl, (NH ₄) ₂ HPO ₄	16-16-16	Apatite, Quartz., CaHPO ₄ , CaSO ₄	NH ₄ NO ₃ . 2KNO ₃ (DS)	6
			(7:3) (NH ₄) ₂ SO ₄ -K ₂ SO ₄ (SS)	4	
			(9:1) NH ₄ H ₂ PO ₄ -KH ₂ PO ₄ (SS)	5	

TABLE 2—CHEMICAL ANALYSIS OF NITROPHOSPHATES, %

Grades (N-P ₂ O ₅ -K ₂ O)	N		P ₂ O ₅			K ₂ O	Ca
	Total	NH ₄ -N	Total	Water-Soluble	Available		
16-13-0	16.1	7.8	14.0	12.04	100.00	—	13.92
13-13-0	13.1	8.18	13.4	5.82	98.65	—	13.90
20-20-0	20.0	10.6	20.0	6.0	99.99	—	10.0
20-18-0	20.34	10.83	17.47	4.47	98.74	—	8.8
23-23-0	23.0	14.0	23.0	18.0	99.50	—	—
24-16-0	24.5	24.2	16.3	11.9	98.15	—	1.73
26-17-0	26.0	16.0	15.0	13.0	99.84	—	1.29
10-10-10	9.8	9.8	10.5	8.87	98.17	10.92	—
10-20-20	10.6	10.6	20.9	20.88	100.00	21.95	—
16-16-16	16.0	10.0	16.0	13.0	99.98	16.0	—

salts to form NH_4Cl , KNO_3 , K_2SO_4 , etc. The formation of various types of double salts and solid solutions is quite remarkable in this case. The double salt, $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$, is one of the major phases present in the products 10-10-10 and 10-20-20. In 16-16-16, in the presence of ammonium nitrate potassium nitrate reacts to form the double salt $\text{NH}_4\text{NO}_3 \cdot 2\text{KNO}_3$. Apart from these, in all the three nitrophosphates containing potash, potassium sulphate is mainly present in the form of a solid solution of different types.

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The extent of crystalline perfection of a few double salts, frequently formed in the manufacture of fertilizers, has been calculated by knowing the lattice constants and density of the crystals with a high precision. A knowledge of the soundness of these crystals provides a better understanding of the mechanism of caking of fertilizers.

Imperfections in the Crystals of Fertilizer Compounds

By V. K. SRINIVASA AND S. K. GHOSH,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

In the manufacture of fertilizers, which are mostly homogeneous crystalline compounds, varieties of double salts and solid solutions—often undesirable materials—are formed either from the usual components or from the extraneous matter in the raw materials. A knowledge of the actual formation of these compounds and the soundness of the crystals so formed not only provides a better understanding of the properties of fertilizers but also aids in the interpretation of undesirable changes in the composition and properties of the products that result from the unsuspected imperfections in the crystals.

Method and Results

In the crystal, large defect concentrations produce changes in lattice constants with corresponding changes in the Bragg angles of x-ray reflection. Such changes in the unit-cell volume and average composition also change the crystal density. Therefore, whether a crystal is sound or has imperfections can be determined by knowing the lattice constants and density of the crystal with a high precision.

The extent of crystalline perfection of a few double salts, frequently formed in the manufacture of fertilizers, has been calculated on the basis of the method developed by Straumanis¹ (Table 1). The lattice constants of the reference compounds are known with a high precision and the density measurements are done with reliable methods. The method involves the determination of molecular weight (M_x) by the formula

$$M_x = NVd/n \quad (1)$$

where N is the Avogadro number (in this case,

$N = 6.02385 \times 10^{23}$), V is the volume of the unit-cell in Å, d is the density and n is the number of molecules per unit cell. The type of imperfection in the crystal lattice is then determined by a comparison with the chemical molecular weight (M). If the difference is D , then:

$M_x - M = -D$ indicates vacant sites.

$M_x - M = +D$ indicates interstitial atoms.

and, $M_x - M = 0$ indicates the crystal is perfect.

The expression $(M_x - M)/M = I$ gives the ratio of the number of imperfect sites to all sites.

In the present case, the uncertainty of an ΔM is determined by

$$\Delta M = \left(\frac{v_1}{v} + \frac{d_1}{d} \right) M \quad (2)$$

where V_1 and d_1 are the uncertainties in the measurement of unit cell volume and density respectively.

Therefore, only if the value of D exceeds ΔM the presence of imperfections in the crystal lattice can be established. Otherwise, the crystal may be regarded as perfect.

Discussion

At the first sight, from Table 1 it seems that the first two compounds have interstitial atoms, but as the value D lies completely within the corresponding limits of uncertainty ΔM , we can regard these crystals as sound. In all other cases, D exceeds the error limits and hence we can suspect imperfections in these crystals. Compounds, such as $\text{NH}_3\text{NO}_3(\text{NH}_4)_2\text{SO}_4$ (1:1) and $4\text{CO}(\text{NH}_2)_2 \cdot \text{Ca}(\text{H}_2\text{PO}_4)_2$, have interstitial atoms and

TABLE 1—DIFFERENCE (D) IN THE MOLECULAR WEIGHTS DETERMINED BY
X-RAY DENSITY MEASUREMENTS AND CHEMICAL DATA

Compound	M_x	M	D	ΔM	$I=D/M$
$3\text{NH}_4\text{NO}_3(\text{NH}_4)_2\text{SO}_4$	372.40	372.290	+0.110	0.2204	—
$\text{SNH}_4\text{NO}_3(\text{NH}_4)_2\text{SO}_4$	292.20	292.232	+0.032	0.1770	—
$\text{NH}_4\text{NO}_3(\text{NH}_4)_2\text{SO}_4$	212.70	212.194	+0.506	0.0862	0.00198
$4\text{CO}(\text{NH}_4)_2\text{Ca}(\text{H}_2\text{PO}_4)_2$	474.90	474.294	+0.606	0.2719	0.00700
$\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	285.55	286.308	−0.758	0.1354	0.00218
$\text{Co}(\text{NH}_4)_2\text{NH}_4\text{Cl}$	112.90	113.555	−0.655	0.0811	0.00507
$\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	328.20	328.428	−0.228	0.2054	0.00007

$\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{NH}_4)_2\text{NH}_4\text{Cl}$, and $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ vacant sites in their lattices.

It has been observed² that in certain crystals the concentration of imperfections due to interstitial or substitutional atoms tends to form a regular nuclei at elevated temperatures. When such defects attain a sizeable proportion, phase segregation may take place. This process is likely to occur in the crystals of $\text{NH}_4\text{NO}_3 : (\text{NH}_4)_2\text{SO}_4$ and $4\text{CO}(\text{NH}_4)_2 \text{Ca}(\text{H}_2\text{PO}_4)_2$, where the imperfections due to the interstitial atoms effect their stability at elevated temperatures. Also, the departure from the ideal composition in some crystals—viz. last three compounds in Table 1—shows that in these crystals some positions are unoccupied. Larger agglomeration of such vacancies may accommodate foreign atoms or absorb water molecules thereby the fine crystalline structure collapses

to form a clogging phase. This type of mechanism is likely to happen in the compounds $\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{NH}_4)_2\text{NH}_4\text{Cl}$ and $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, which are the caking phases in fertilizers during the process or storage.

Acknowledgement

The authors' thanks are due to Dr. B. K. Banerjee, Addl. Superintendent, Physical Research Wing, for his valuable suggestions and constant encouragement in this work.

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Particle Size of Solid Aggregates by Beta—Backscattering

By S. K. BANERJI, A CHATTERJEE AND S. K. DAS,

*Planning & Development Division,
The Fertilizer Corporation of India Ltd., Sindri, Bihar*

Analysis and determination of particle size are of immense importance in the chemical technology. It is known that activity of fertilizer catalysts in the form of solid aggregates has got considerable dependence on the particle size. Moreover, to achieve the free flowing condition of fertilizers they must be coated with some anticaking materials. These coating agents must have strong adhesive properties and should cover the fertilizer granules uniformly. Particle size plays a vital role from this point of view, because neither uniform coverage nor strong adhesion can be obtained from particles of different sizes and shapes. In the present communication, determination of particle size of solid aggregates in the form of (i) metal oxide system (similar to the oxide system used in fertilizer catalysts) and (ii) dolomitic limestone (a fertilizer coating agent) have been discussed utilising the β -backscattering from a $\text{Sr}^{90}\text{-Y}^{90}$ source. Though the other methods¹ are also used for the same purpose the present method has been preferred because of its simplicity without foregoing accuracy.

Experimental

The experimental samples were crushed and sieved to different mesh sizes ranging from 16 to 300 B.S.S. and were kept in a desiccator to avoid moisture absorption. A glass tube having an area of cross-section 3.8 cm^2 , fitted with a mica window of thickness 7.25 mg/cm^2 was used as a sample holder. Mica window was preferred because of its low atomic number which consequently reduces the overall background scattering. The sample tube was positioned in a thick perspex mount above a $0.5\text{ mc Sr}^{90}\text{-Y}^{90}$ β -source. The source was contained in

a small glass capsule embedded in an annular lead ring surrounding an end-window G.M. tube of window thickness 1.5 mg/cm^2 , which in turn is connected to a counting set up. The spatial relationship between the source, counter, and the sample holder was always kept fixed at the best feasible geometry². The window of the G.M. tube and the top of the source pit in the lead ring, which also gave proper collimation of the source, were in the same horizontal plane. The thickness of the lead ring surrounding the G.M. tube was sufficient to shield direct radiation from the source. The experimental samples in different particle sizes and weights were taken in the sample tube and backscattered count rates were measured by the G.M. counting set up.

Results and discussions

The variations of count rate with the thickness of the scattering material for different particle sizes are indicated in Figs. 1 & 2, for metal oxide system and dolomitic limestone respectively. It is clear from the curves that with the increase of thickness the count rate is also increasing regularly and tends to attain a saturation. The dependence of backscattering on the particle size of the target for a fixed thickness is apparent from the Figs. 3 & 4. For a certain thickness of the scatterer the count rate is found to increase linearly with the fineness of the scattering particles. The curves shown in Figs. 3 & 4 can be directly used to measure the particle size of corresponding material from the backscattered count rates. Thus calibrating for thickness and count rate this method can be extended to other solid materials also for particle size measurements. The process of β -back-

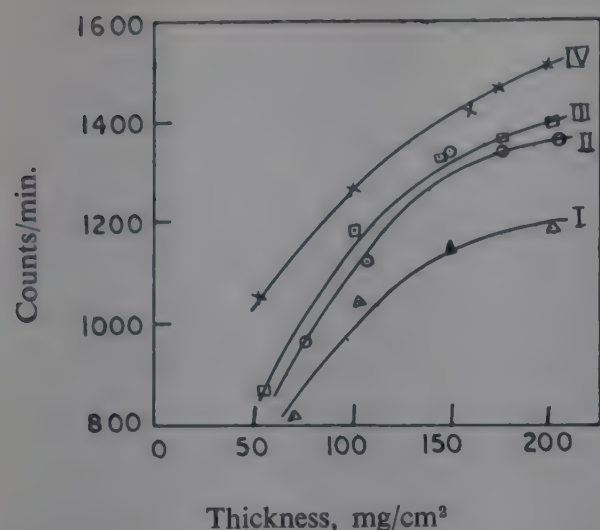


Fig. 1—Variation of Count Rate with Thickness of Metal Oxide System

I—Mesh Size 16- 60 BSS
 II—Mesh Size 60-100 BSS
 III—Mesh Size 100-200 BSS
 IV—Mesh Size 200-300 BSS

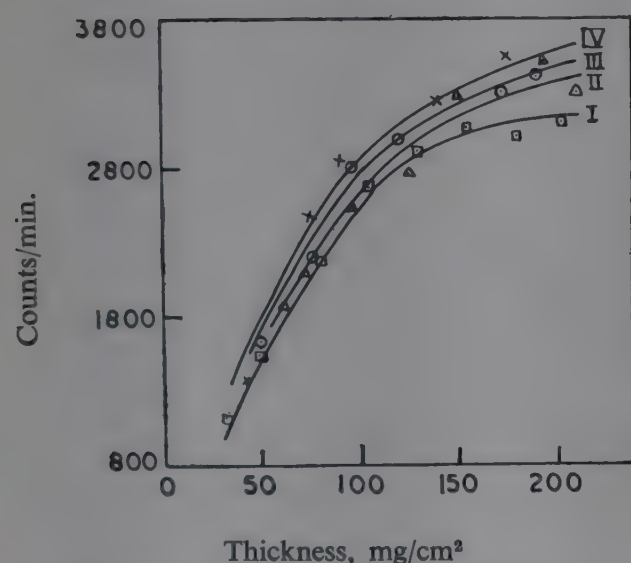


Fig. 2—Variation of Count Rate with Thickness of Dolomitic Limestone

I—Mesh Size 60-100 BSS
 II—Mesh Size 100-120 BSS
 III—Mesh Size 120-200 BSS
 IV—Mesh Size 200-300 BSS

scattering is a complex one and has already been discussed in details elsewhere^{3,4}. However, the effective atomic number of the scattering material should be more than 16 for the applicability of this method⁵. The metal oxide system and dolomitic limestone used in the present experiment satisfy the above condition. The counting has been confined up to the saturation limit of the backscattered β -radiation as the present method is effective only up to that.

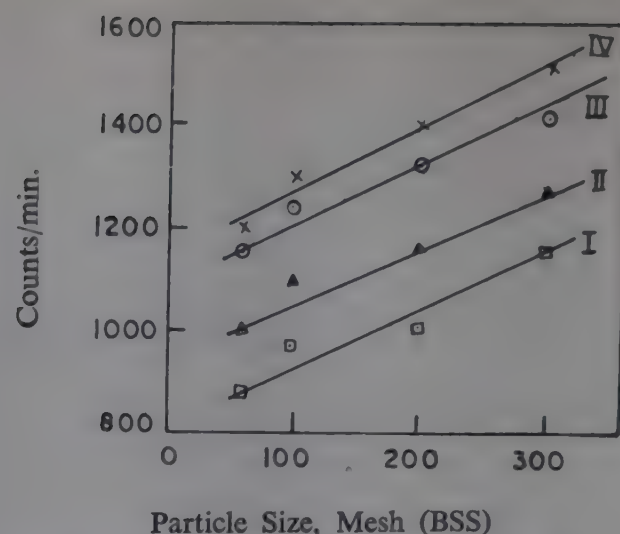


Fig. 3—Variation of Count Rate with Particle Size for Metal Oxide System

I—Thickness 75 mg/cm²
 II—Thickness 100 mg/cm²
 III—Thickness 150 mg/cm²
 IV—Thickness 200 mg/cm²

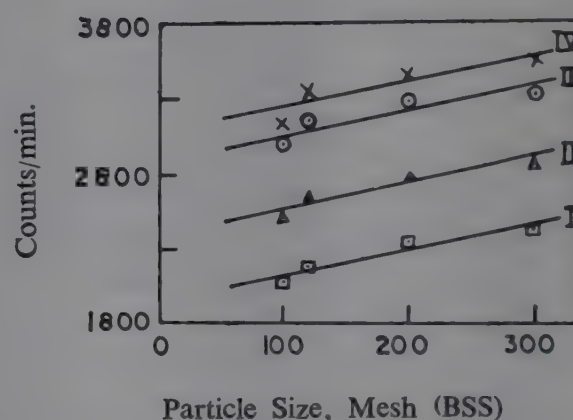


Fig. 4—Variation of Count Rate with Particle Size for Dolomitic Limestone

I—Thickness 75 mg/cm²
 II—Thickness 100 mg/cm²
 III—Thickness 150 mg/cm²
 IV—Thickness 200 mg/cm²

Acknowledgement

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In the present work urea-based N-P formulations in the granular form have been prepared in the laboratory and the hydrolysis of urea, extent of reversion of water soluble P_2O_5 and the percentage of ammonia retained in the granular products have been estimated. Influence of temperature and duration of heating on the above aspects have been studied. It has been found that the addition of ammonium sulphate along with urea decreases the extent of hydrolysis as well as the reversion of water soluble P_2O_5 to the water insoluble form. The hygroscopicity and the crushing strength of various samples have been determined. Crushing strength of the various samples at 1 per cent moisture level is found to decrease with decreasing proportion of urea used in the formulations.

Urea in N-P Formulations

By S. VARMA, D. P. VASUDEVA AND K. N. CHOUDHARY,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Urea in a few years' time would be abundantly available in the country. Utilization of urea in combination with phosphatics towards the production of N-P fertilizers would be an attractive and desirable proposition as one of the best ways to ensure balanced fertilization is to make available multinutrient fertilizers. According to Jacob and Uexkull¹ urea is far from an ideal fertilizer as far as its mixing with other fertilizers is concerned and should therefore be blended with other constituents shortly before use. Bulk blends containing urea with normal or triple super phosphate have a tendency to lose its free flowing characteristics and become wet and sticky². Frazier³ conclusively proved that this rapid deterioration is due to the fact that urea forms an adduct with mono-calcium phosphate and thereby releases its water of crystallization according to the following equation:



The released water forms saturated solution of soluble constituents and generates enough liquid phase because of high solubility of urea to cause stickiness and caking. Ammoniation of the granulated TSP prevents the Urea-MCP adduct formation but the water solubility is reduced to approximately 50 per cent⁴.

Composite multinutrient granules have distinct advantages over blended fertilizers, as these can be bagged, stored for a longer period and can be transported to distances without any possibility of segregation of the constituents and facilitates accurate and uniform distribution. Problems that arise when attempts are made to granulate urea with TSP or SSP consist of (a) sudden release of water of crystallisation which interferes in the process of granulation (b) hydrolysis of urea during processing and to a lesser extent during storage causing loss of nutrient and (c) reversion of water soluble P_2O_5 into the water insoluble form. At TVA (U.S.A.) granulated mixtures of urea with TSP were prepared by a novel method². Cured TSP with recycle fines was ammoniated in a rotary ammoniator-granulator by the addition of anhydrous ammonia and water to the rolling bed. To the ammoniated TSP in the same equipment, 96 to 99 per cent urea solution was sprayed. Good granules were obtained but the water solubility was reduced to 50 per cent.

Clur et al⁵ reported that the hydrolysis of urea during processing of N-P formulations depended on the temperature and retention time in the dryer, with the temperature of granules at 100°C and retention time of 15 min. 3.8 per cent urea was hydrolysed. Phillips et al⁶ found that with 12-12-12 fertilizer with urea as one of

the components hydrolysed to the extent of 4, 8 and 32 per cent in 60 days at 38°, 54° and 82°C respectively. No appreciable hydrolysis occurred during storage at 30°C or below. Jenson⁷ studied the hydrolysis of urea in 3-16-16, 10-10-0 and 5-20-20 where nitrogen solution of ammonia and urea were used as a nitrogen carrier. Product temperature in the ammoniator was in the region of 66-93°C with a residence time of 10 and 15 min. in the counter-current dryer in the temperature range of 66-121°C. It was found that with a total residence time of 25 minutes in the ammoniator and the dryer, the extent of nitrogen loss was insignificant. According to Jewell⁸ drying of granules to a temperature of 90°C could be tolerated with urea and superphosphate based N-P-K fertilizer provided that the retention time in the dryer did not exceed 15 min. He further suggested that the storage temperature should not exceed 35°C.

In the present work urea based N-P formulations have been prepared in the granular form in the laboratory and the hydrolysis of urea, extent of reversion of water soluble P₂O₅ into water insoluble form and the loss of nutrient resulting from the hydrolysis of urea has been estimated in various formulations. Influence of temperature and duration of heating on the above aspects have been studied and hygroscopicity and the crushing strength of the granular products determined.

Experimental

Materials Used: Urea—Fertilizer grade prilled fertilizer containing 46.2 per cent nitrogen and 0.51 per cent biuret. T.S.P.—Total P₂O₅ 50 per cent, water-soluble P₂O₅ 47.0 per cent. Citrate-insolubles and free phosphoric acid in traces. N.S.P.—Total P₂O₅ 21.4 per cent; water-soluble P₂O₅ 18.7 per cent; Citrate-insoluble P₂O₅ 0.70 per cent. Free phosphoric acid in traces.

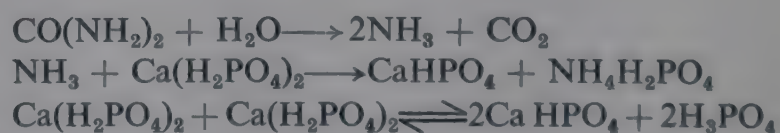
Granulation was carried out by heating the sample with minimum amount of water to a definite temperature on oil bath to a consistency which could be granulated in a small paddle type granulator. Since the extent of hydrolysis of urea and accompanying reversion of water soluble P₂O₅ is dependent on the temperature and duration of heating during processing, temperature was kept constant except when the effect of temperature was studied. Changes in the formulations necessitated heating the samples to varying periods of time but an attempt was made to study the effect of variables by keeping the time as close as possible. Granular product was screened to 4 to 6 mesh size for crushing strength determinations and 10 to 14 for other studies. The duration of heating during processing was in the range of 20 to 40 minutes and was considered adequate as far as

the retention time of the granules in a granulator and the dryer is concerned and the samples were finally dried at the room temperature over vacuum desiccator. The product was then analysed for total and water soluble P₂O₅. Urea was estimated by urease method. In the samples containing ammonium sulphate and urea, ammoniacal nitrogen was indirectly estimated from the difference between the total nitrogen and the nitrogen present in the form of urea.

For control of temperature and the duration of heating a separate set of experiments were conducted with small quantities of pulverized samples conforming to a particular grade with similar quantity of water in each of the samples and heated in an oil thermostat for predetermined period of time after which extent of reversion of P₂O₅ and the extent of nitrogen loss was determined in each case. Moisture uptake in 4 hours was determined for some of the typical granular samples by exposing them in desiccator filled with saturated solution of ammonium sulphate. The weight required to crush a single granule of 4 to 6 mesh size was taken as its crushing strength. Results given are an average of six determinations. Crushing strength was determined in each case of the samples containing 1 per cent moisture.

Discussion

The reversion of water-soluble P₂O₅ into the water insoluble form and the loss of ammonia occurring in the formulation containing urea and TSP/NSP arise mainly on account of the hydrolysis of urea. The hydrolysis of urea is catalysed both by acids and alkalies and is influenced by the presence of inorganic salts⁸. Lundstrom and Whittaker⁹ found that monocalcium phosphate accelerated the hydrolysis of urea. Impurities present in rock phosphate also have significant effect on the rate of hydrolysis of urea. The reversion of water-soluble P₂O₅ to water-insoluble dicalcium phosphate during granulation and drying of urea-TSP/NSP product is on account of the following reactions.



The equilibrium of the last reaction is shifted towards the formation of dicalcium phosphate under alkaline conditions. The formation of water insoluble dicalcium phosphate ultimately depends on the availability of soluble calcium. It was, therefore, considered worthwhile to study the effect of the addition of ammonium sulphate to the urea-TSP/NSP formulations since ammonium

TABLE 1—HYDROLYSIS OF UREA AND % NH₃ RETAINED

Sample No.	Formulation in Parts and Grade		Temperature & Time of Processing	Hydrolysis of Urea, %	NH ₃ Retained, %	Reversion of Water Sol. P ₂ O ₅ , %	Citrate insolubles
PU ₁	NSP	219	110±2°C	17.44	83.11	57.7	0.70% No change
	Urea	100	30 min.				
	(14.4-14.4-0)						
PU ₂	TSP	200	110±2°C	16.41	80.2	52.5	traces
	Urea	220	30 min.				
	(24-24-0)						
PUA ₁	TSP	100	110±2°C	13.91	84.2	34.3	traces
	AS	52.5	30 min.				
	Urea	85.5					
	(21-21-0)						
P ₁ UA ₃	TSP	100	110±2°C	7.52	85.1	18.9	traces
	AS	50	30 min.				
	Urea	86					
	(21-21-0)						

P series: Granular formulations in which all the constituents are mixed at the same time.

P₁ series: Granular formulations in which Urea is added later to the slurry of ammonium sulphate and TSP.

sulphate would react with monocalcium phosphate to form monoammonium phosphate and less soluble calcium sulphate. In some of these samples, urea, ammonium sulphate and TSP were mixed at the same time. In other samples urea was added later to the slurry of ammonium sulphate and TSP.

Results as given in Tables 1 and 2 indicate that (1) The extent of reversion of water soluble P₂O₅ into the water insoluble form increases with the increase in the extent of hydrolysis of urea; (2) The reversion is limited to the water insoluble but citrate soluble dicalcium phosphate; (3) In the presence of ammonium sulphate, extent of reversion and hydrolysis of urea are less. The decrease in the reversion is more when urea is added later to the slurry of ammonium sulphate and TSP than in case where all the constituents are mixed at the same time; (4) The decreased reversion is not entirely due to the decrease in the proportion of urea used is clearly observed from the results given in Table 2 in which the sample PU₃ containing only urea and TSP in proportion 67:124 undergoes greater reversion than PUA₁ where the proportion of urea to TSP is 85.5:100 and contains in addition 52.5 parts of ammonium sulphate under similar conditions of temperature and processing time. (5) Most of the ammonia evolved resulting from the hydrolysis of urea was retained in the product as ammonium salt. In the case of sample containing urea and superphosphate over eighty per cent of ammonia released was retained on account of the following reactions.

TABLE 2—GRANULATION OF VARIOUS FORMULATIONS AND REVERSION OF WATER-SOLUBLE P₂O₅

Sample No	Formulation in Parts and Grade		Temperature (°C) and Duration of Heating	Reversion of Water-soluble P ₂ O ₅ , %
PU ₁	NSP	219	110 ± 2	57.7
	Urea	100	30 min.	
	(14.4 - 14.4 - 0)			
PU ₃	TSP	124	110 ± 2	47.6
	Urea	67	30 min.	
	(16.1 - 32.5-0)			
PU ₄	TSP	100	110 ± 2	50.3
	Urea	200	30 min.	
	(30.7 - 16.7 - 0)			
PUG	MAP	77	110 ± 2	15.4
	Urea	104	30 min.	
	Gypsum	58		
	(23.9 - 20.0 - 0)			
PUA ₁	TSP	100	110 ± 2	34.3
	AS	52.5	30 min.	
	Urea	85.5		
	(21.0 - 21.0 - 0)			
*PUA ₂	TSP	100	110 ± 2	32.9
	AS	44	30 min.	
	UREA	89		
	(21.4 - 21.4 - 0)			
P ₁ UA ₃	TSP	100	110 ± 2	18.9
	AS	50	30 min.	
	Urea	86		
	(21 - 21 - 0)			

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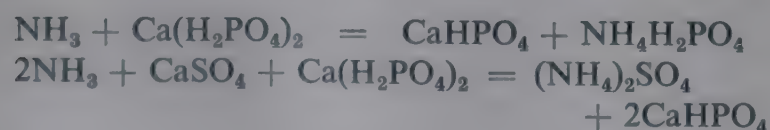
TABLE 2—GRANULATION OF VARIOUS FORMULATIONS
AND REVERSION OF WATER-SOLUBLE P₂O₅

(Continued from previous page)

Sample No	Formation in Parts and Grade	Temperature (°C) and Duration of Heating	Reversion of Water-soluble P ₂ O ₅ , %
*PUA ₄	TSP	75	46.3
	As	33	
	Urea	138	
	(28.6 - 15.2 - 0)	110 ± 2 30 min.	
P ₂ UA ₆	TSP	50	33.2
	AS	100	
	Urea	56	
	(22.7 - 12.1 - 0)	100 ± 2 40 min.	
P ₃ UA ₇	TSP	75	32.9
	AS	30	
	Urea	150	
	(30.0 - 14.7 - 0)	100 ± 2 50 min.	
P ₄ UA ₈	TSP	75	20.7
	AS	66	
	Urea	123	
	(26.7 - 14.2 - 0)	100 ± 2 50 min.	
*P ₅ UA ₉	TSP	100	7.1
	AS	44	
	Urea	89	
	(21.4 - 21.4 - 0)	90 ± 2 60 min.	
P ₆ UA ₁₀	TSP	100	7.1
	AS	52.5	
	Urea	85.5	
	(21 - 21 - 0)	90 ± 2 60 min.	
P ₇ UA ₁₁	TSP	100	6.5
	AS	35	
	Urea	93	
	(21.9 - 21.9 - 0)	90 ± 2 60 min.	
PUA ₁₂	TSP	100	6.3
	AS	52.5	
	Urea	85.5	
	(21 - 21 - 0)	90 ± 2 45 min.	
PUA ₁₃	TSP	100	13.1
	AS	35	
	Urea	93	
	(21.9 - 21.9 - 0)	90 ± 2 60 min.	

In P₁ to P₇ Samples, slurry of AS and TSP was made at the temperatures indicated and urea was added later. In all other cases the constituents were mixed at the same time (P series).

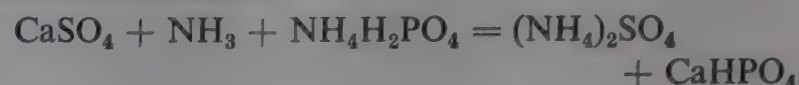
* In these formulations ammonium sulphate is in stoichiometric proportion to MCP.



The decrease in the extent of reversion in samples containing ammonium sulphate is due to the removal of calcium ions as calcium sulphate on account of following reaction.



The formation of dicalcium phosphate cannot be totally prevented because of the increased solubility of calcium sulphate under alkaline conditions in the presence of ammonia formed in situ from the hydrolysis of urea as shown below:



This was confirmed by processing monoammonium phosphate, calcium sulphate and urea together as shown in Table 2 (sample PUG) in which case the extent of reversion of water-soluble P₂O₅ was about 15 per cent at 110°C with 30 min. as processing time. The difference in the extent of reversion in the case of samples in which urea is added later and in those mixed at the same time indicate that the reaction between ammonium sulphate and monocalcium phosphate may not be completed when urea is getting hydrolysed into ammonia and carbon dioxide.

The effect of processing temperature on the extent of reversion is clearly seen from the results given in Table 3. Temperature has a profound influence and the extent of reversion at 90°C is considerably less than at 110°C. Unfortunately the influence of processing time is not clearly discernible from the results because the formulations required varying processing time for the formation of granular product.

TABLE 3—EFFECT OF TEMPERATURE ON % REVERSION
OF WATER-SOLUBLE P₂O₅

Sample No.	Formulation in Parts and Grade	Duration of Processing (20 mins.) at Temperature		
		110°C % reversion	100°C % reversion	90°C % reversion
P ₀ U	TSP	53.2	30.3	16.6
	Urea			
	(24 - 24 - 0)			
P ₀ UA ₁	TSP	34.3	19.4	9.5
	AS			
	Urea			
	(23.4 - 20.3 - 0)			
P ₀ UA ₂	TSP	28.2	14.5	6.2
	AS			
	Urea			
	(23.4 - 19.8 - 0)			
P ₀ UA ₃	TSP	30.1	17.5	12.2
	AS			
	Urea			
	(23.3 - 19.2 - 0)			

All the constituents added at the same time.

TABLE 4—HYGROSCOPICITY & CRUSHING STRENGTH OF GRANULES

Sample No.	Formulation & Grade	Temperature & Time of Processing	Moisture Uptake in 4 hr. mgm/cm ²	Critical Relative Humidity (Theoretical) Approximate, %	Crushing Strength of Granules, 1% moisture in kg.
PU ₁	NSP Urea (14.4-14.4-0)	219 100 110±2°C 30 min.	8.22	61	8.6
PU ₂	TSP Urea (24-24-0)	200 220 110±2°C 30 min.	8.03	57	9.2
PUA ₁	TSP AS Urea (21-21-0)	110 32.5 85.5 110±2°C 22 min.	8.33	58	7.5
PUA ₂	TSP AS Urea (21.4-21.4-0)	100 44 89 110±2°C 30 min.	9.25	54	8.1
PUA ₃	TSP AS Urea (13.3-26.7-0)	124 74 33.5 110±2°C 25 min.	5.80	63	7.6

All the constituents added at the same time.

In Table 4 the hygroscopicity of some of the typical granulated mixtures and their crushing strengths are given. From the amount of moisture absorbed in 4 hours, the critical relative humidity has been evaluated on the basis of following relationship¹⁰ using ammonium nitrate as a reference sample.

$$h_o = \frac{Q_1 h_x - Q_2 h_A}{Q_1 - Q_2}$$

Where Q_1 and Q_2 are the amounts of moisture absorbed in 4 hours by ammonium nitrate and of the sample whose CRH is to be determined when subjected to the controlled relative humidity h_o , h_A and h_x are the CRH of ammonium nitrate and of the sample respectively.

It is seen that the critical relative humidity (CRH) varies between 54 and 61 per cent. The least hygroscopic Urea-TSP product is of grade 13.3-26.7-0 where the proportion of urea is less than in grades, 21-21-0 or 24-24-0. There is, however, no significant difference in the hygroscopicity of the latter samples. Crushing strengths of granules containing 1 per cent moisture for the samples prepared at 110°C are given in the Table 4.

Crushing strengths of granules appear to increase with an increase in the proportion of urea used. Experiments with N-P-K formulations are in progress.

Acknowledgement

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A method based upon counter-current washing technique has been devised in this laboratory using a simple cell for the extracting of lime and removal of slimes from calcined Indian rock phosphates, which contain a considerable amount of calcium carbonate along with clayey impurities. In the present investigation, P_2O_5 contents in rock phosphate samples from Udaipur-Kanpur and Jaisalmair areas of Rajasthan could be enriched from 12.90 to 30.50; 14.20 to 27.22 and from 11.56 to 15.70 per cent in concentrates with P_2O_5 recoveries of 95.8, 67.0 85.3 per cent respectively in concentrates.

A Counter-Current Washing Technique for Lime and Fine Clay Removal from Calcined Rock Phosphates

By M. K. BARDHAN, T. R. LODHA, Y. R. RAO
AND A. K. ROY,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

In a previous communication¹ it was shown that an Indian rock phosphate could be beneficiated by removal of carbon dioxide by calcination followed by quenching in water. A method has now been evolved in this laboratory based on counter-current washing technique using a simple cell for the extraction of lime and removal of slimes from calcined rock phosphates, which contain carbonaceous and clayey impurities. These impurities are mostly carried over with wash water in the form of fine suspensions and the concentrate that remains after washing becomes enriched in P_2O_5 .

The principle underlying the process is that the materials are partially disintegrated by the initial calcination and quenching in water. The disintegrated mass is then made into a pulp and washed in the cell by counter-current principle. Particles of finer sizes and lower densities are stripped off from the main pulp in the form of fine suspensions by the combined effect of the centrifugal force and upward thrust of water, self-created by injecting water through a fine jet at the bottom which is aligned with the curvature of the cell. The water impinges on the side of the cell and initiates some vortex action which helps to carry the finer particles upward. The impurities, mostly being in the finer sizes, are carried with the stream of water as an overflow.

Procedure

A weighed amount of rock phosphate is calcined at 980-1000°C for about 2 hours and immediately quenched in a steel vessel containing only demineralized water. The pulp is constantly agitated during the leaching process and its density is generally maintained at 12 to 15 per cent. The whole pulp is then quickly transferred to the counter-current cell where it is further diluted with demineralized water giving a pulp density of 9 to 10 per cent. The pulp is then agitated at 1500-1600 rpm for 15 to 20 min. when the adhering fines start coming off and form a slurry. The stirrer speed is then reduced to 180-190 rpm and water is injected through the bottom of the cell. The flow of water and stirrer speed are set at such a rate that there is a minimum turbulence in the upward flow of water and a fine suspension of pulp is maintained. The overflow is collected in a vessel and the underflow containing concentrate is recycled. The whole process of washing and recycling is continued for 25-30 min. till the supernatant overflow becomes clear.

Description of Apparatus

The apparatus (Fig. 1) consists of a cylindrical pyrex glass tube (A) of above 12 in. length and 2 in. internal diam. The cell is rounded at the bottom with which a

glass stop cock (B) is attached for taking out the concentrate, collected at the bottom. A side glass tube (D) of

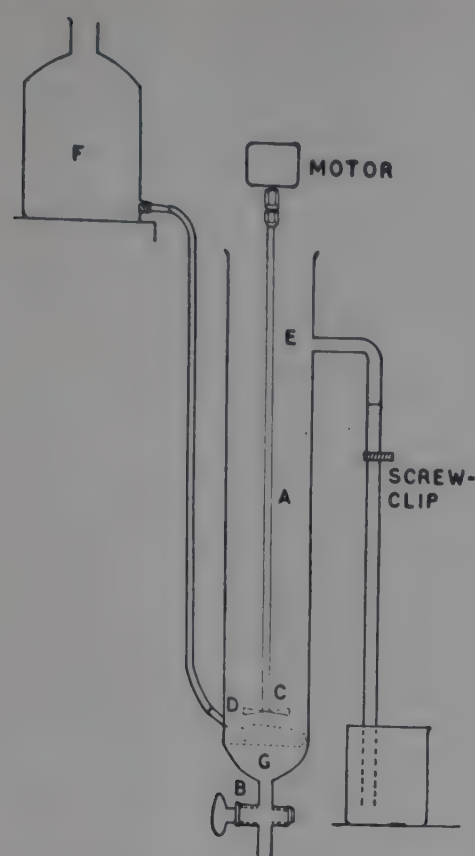


Fig. 1—Apparatus for Extracting Lime and Removal of Slimes from Rock Phosphate

6-8 mm. diam. with fine jet at one end of 0.3-0.5 mm. bore is inserted through the side of the cell tube at a height of 1 in. from the bottom of the cell. The wider end of the side tube is connected with the source of water supply and its fine jet end reaches the bottom of the cell tube in the form of a curvature similar to and aligned with the inner curvature of the cell tube. The impeller of the glass stirrer (C) is of four-bladed horizontal-type having a diam. of 1 in. and set at 90° to each other. The impeller is kept at middle of the cell and the height is adjusted slightly above the jet. The overflow is discharged through the side tube E about 2 in. below the top.

Experimental Results

Important Test Results with Different Samples: The results are tabulated below (Table 1).

Discussion

It may be seen from the results (Table 1), that both Udaipur-Kanpur and Jaisalmer rock phosphates vary in their composition and their upgradation is possible by this process to a certain extent depending on the nature and amount of impurities present in them. This is more pronounced where carbonate is greater in quantity.

TABLE 1—TEST RESULTS WITH DIFFERENT SAMPLES OF ROCK PHOSPHATE FROM RAJASTHAN
(wt. of sample taken = 30 g. in each case)

Tests	Udaipur-Kanpur, Sample I (P ₂ O ₅ 12.9%)	Udaipur-Kanpur Sample I	Udaipur-Kanpur Sample II (P ₂ O ₅ 14.22%)	Jaisalmer Sample I (P ₂ O ₅ 11.56%)
	(a)	(b)	(c)	(d)
Chemical Analysis, %				
P ₂ O ₅	12.9	—	14.22	11.56
SiO ₂ + Insoluble	5.1	Same as of under column (a)	8.77	26.01
CaO	44.3		43.03	37.35
CO ₂	21.0		21.56	17.20
MgO	11.0		—	—
R ₂ O ₃	2.1		2.07	7.04
Calcination Loss at 980-1000°C, %	28.8	28.1	25.6	16.40
Original P ₂ O ₅ content, %	12.9	12.5	14.2	11.56
Size of the Feed, mesh size (B.S.)	— 52 (90.5%)	— 52 + 200 (77.4%)	— 52 (99.5%)	— 60 (99.5%)
P ₂ O ₅ Content after Processing and Drying, %	30.0	30.48	27.22	15.7
Sp. Gr. of the Concentrates	3.063	3.011	2.824	2.754
P ₂ O ₅ Content of Tails, %	9.01	6.39	7.56	5.38
Sp. Gr. of Tails	2.284	2.274	2.824	2.620
Approx. Recovery (calculated on P ₂ O ₅ basis), % in Concentrate	75.0	95.8	67	85.3
Flow Rate of Overflow, ml/min.	145-150	135	135	125
Speed A* and B,** rpm	1580,190	1580,190	1550,185	1500,180

* at the time of initial agitation of pulp.
** when water jet was also opened.

Note: Sp. gr. in all cases measured in a saturated solution of CaO at room temperature and then multiplied by its density.

It may, however, be presumed from the above results that more than 90 per cent of the carbonate could be eliminated by this technique which will be possible only if the impurities, after the initial calcination and quenching, remain in the finer fractions. The original feed sample taken for processing is of a particular size [-52 mesh (B.S.)], which was found to be one of the suitable sizes after some preliminary investigations. In the case of sample (b) a slight variation in the original feed size was made (77.4 per cent $-52 + 200$) and it underwent the same process treatment. It may be seen that though P_2O_5 content in the final concentrate is

enriched only to 0.5 per cent more, the recovery has improved from 75 to 95.8 per cent. Hence it is apparent from the above findings that a portion of the impurities goes to the finer fractions at the initial grinding stage and that a selective sizing of the original feed may help in the better upgradation and recovery of such types of rock phosphate.

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Polarization data obtained with mild steel in the degasification section water in an ammonia plant, in presence and absence of different inhibitors, have shown correlation with weight-loss data obtained earlier.

Polarization Characteristics of Mild Steel in the Degasification Section Water in An Ammonia Plant

By Y. K. VARMA, G. R. BHATNAGAR AND A. K. ROY,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

In an earlier communication¹, results were given of weight-loss experiments carried out with mild steel in the degasification section water in an ammonia plant, in presence and absence of various inhibitors. Further studies have been carried out on the polarization characteristics of mild steel under the same conditions, since such data throw much light on the mechanism of corrosion and inhibition of a metallic system. The results are reported in this paper.

Experimental

Polarization experiments were conducted at 40°C with mild steel test coupons immersed in freshly collected and filtered degasification system water. The water was

taken in an open glass vessel placed in a thermostat. Rectangular mild steel coupons of size $4.5 \times 1.0 \times 0.2$ cm. were taken and connected to a rod of the same composition through a hole drilled at the top of the coupon. The surface was finally prepared on 'O' emery and degreased. The top portion of the electrode was insulated by pliocene cement or candilla wax to keep a definite surface area available as a half cell. The other half cell for the purpose of polarization was a square platinum electrode, the two being held 1.5 cm. apart. Potential measurements were made with respect to saturated calomel half cell. Impure carbon dioxide from the degasification system was constantly bubbled through the solution as described in the earlier paper¹. Potential

on the other hand, found tetraploid *Anona* to grow faster and flower earlier than its diploid progenitor. Hence, the growth of tetraploid Pusa Seedless and Bharat Early Grapes (on diploid root system) as found in the present study is of interest.

Cane and tendril became stouter and thicker in tetraploids. The increase in thickness of these plant parts is due to increase in cell size by tetraploidy. Internodes were shortened by tetraploidy. The shortened internode is a known feature of polyploids and Dermen and Bain³ found it, along with other morphological characteristics, as a good criterion for total polyploidy in cranberries. Tetraploid plants had thicker, broader and deep green leaves with increased number of serrations and thicker petioles (Table 2). By studying these deviations one can suspect fairly accurately in grape whether tetraploidy has been induced or not. Increased leaf serrations in tetraploids may probably be a factor related to increased leaf area. Dermen² suggested that U-shaped petiolar sinus of tetraploid muscadine grapes (*Vitis rotundifolia*) was a very reliable index of induced tetraploidy. But when this character was carefully studied in all the eleven induced tetraploid varieties, no such clear cut modification could be observed. Although some tetraploid leaves showed a tendency towards this modification (U-shaped petiolar sinus), probably due to the reduction in petiolar sinus by increased leaf area in that part of the leaf, it was not invariably associated with tetraploidy. Because many leaves from diploid plants also exhibited a sort of U-shaped petiolar sinus prob-

bly due to growth modifications and internal tissue displacement in early stages of leaf ontogeny. So this character was not found to be a useful index for identifying tetraploid twigs morphologically. The data on the anatomy of different plant parts like leaf, stem, petiole and tendril indicated that tetraploid grapes had bigger cell size than their diploid counterparts and all the altered physiological changes that are associated with polyploids are attributed to increased cell size⁹.

Acknowledgements

The author is grateful to Dr. S. K. Mukherjee, the then Head of the Division of Horticulture, I.A.R.I., New Delhi, for his invaluable guidance during the investigation and also for writing this paper and to Dr. H. K. Jain, Head of the Division of Genetics, I.A.R.I., for constant help.

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In this article, the author describes the application of earthing transformers which would give effective earths for stabilizing the system voltages under earth fault conditions and to ensure selective and positive earth fault relaying. It has also been described how for effectively grounded neutrals, the continuous kVA ratings of such earthing transformers could be worked out. The use of underrated earthing transformers, where the element of expense comes in, would permit low earth fault currents, which could disrupt efficient control and protection and introduce dangerous transient over-voltages resulting in insulation failures.

Use of Earthing Transformer

By R. C. TALWAR,

*Fertilizer Corporation of India, Ltd., Durgapur,
(W. Bengal)*

Earthing transformer is an apparatus which creates neutral for earthing either solidly or through an impedance depending upon the restraint to be employed on the flow of earth fault current. It finds its use in systems where Delta-connected apparatus is encountered. It may be necessary to operate such systems or portions thereof either solidly earthed or grounded through reactance or resistance.

In the event of a single-line-to-earth fault, the neutral point tends to shift and the line-to-ground voltage of the unfaulted phases rises. The degree to which this rise in voltage occurs depends on the ratio of zero sequence to positive sequence impedance in the circuit. In the case of ungrounded-systems, the line-to-neutral voltage rises to line-to-line voltage. Similarly, with high resistance and reactance grounding the line-to-neutral voltage could rise to line-to-line voltage depending upon the amount of resistance or reactance in the grounding circuit. The switching surges on such systems may give rise to voltages which may be many times line-to-line voltage. The voltage stabilisation on such systems, therefore, becomes a problem. In solidly or effectively grounded system, however, the voltage rise under fault condition is bound down to certain limits and the protection could be ensured to be effective. The earth fault relaying could also be selective and positive.

Earthing transformer could have a Star-Delta or zig-zag star winding, the latter being more commonly used. In a case study of a power system 31.5 MVA. 132/11 kV Star-Delta power transformer is proposed to be installed with 15 per cent impedance and to create neutral on the 11 kV side of the power transformer zig-zag star earthing transformer which would limit the

earth-fault current to 300 Amp. is contemplated to be erected.

Short-time kVA rating of such an

$$\text{Earthing transformer} = \frac{11}{\sqrt{3}} \times 300 = 1900 \text{ kVA}$$

Such a rating is normally meant for one minute unless some other time is specified.

$$\begin{aligned} \therefore \text{Equivalent continuous KVA rating} \\ &= 1900 \times 0.104 \\ &= 197.6 \text{ kVA or say } 200 \text{ kVA,} \end{aligned}$$

where 0.104 is a factor¹ to obtain equivalent continuous kVA rating of three-phase earthing transformers designed for one minute short-time rating.

The study which follows gives the effect of such an earthing transformer on the system. This earthing transformer will have its star point solidly grounded.

$$\begin{aligned} \text{System three-phase short-circuit current} &= \frac{350 \times 1000}{\sqrt{3} \times 11} \\ &= 18400 \text{ Amp.,} \end{aligned}$$

where 350 MVA is the declared short-circuit level of the system when two transformers 31.5 MVA each are running in parallel and it is not considered to be an infinite bus.

A system is said to be 'effectively grounded', if the

$$\text{ratio } \frac{X_0}{X_1} \text{ does not exceed } 3 \text{ and } \frac{R_0}{X_1} \text{ does not exceed } 1,$$

where X_0 , X_1 and R_0 are Zero sequence reactance, positive sequence reactance and Zero sequence resis-

tance respectively of the circuit². Now for $\frac{RO}{X1} = 1, \frac{XO}{X1} = 3$ and $\frac{X1}{X2} = 1$, single line-to-earth fault current is

approximately 0.6 times the three-phase short-circuit current. This shows that with the earth fault current limited to 300 Amp. against three-phase short-circuit current of 18400 Amp., the system cannot be taken as effectively grounded. In fact such a system could precisely be considered as high-reactance grounded.

It has been observed that on systems of lower voltage, say upto and including 33 kV, ground relaying plays an important role in the selection of mode of grounding, if for instance a high resistance earth fault of 10 ohms or above is encountered. In that event, if the earth fault current is already limited to 300 Amp. by the use of small earthing transformer the actual earth fault current with 10 ohms fault resistance will go down so low and zero sequence voltage will be reduced so much that the directional ground relaying will become utterly ineffective.

The zero sequence impedance increases more rapidly than the positive and negative sequence impedances along the line and so, as the fault moves away from the source of supply, the ground fault current may fall to such an extent that it becomes non-discriminating or even practically non-existent. The positive and selective ground relaying, therefore, becomes impossible.

The alternative would be to have a Delta-Star instead of Star-Delta or Star-Star-Delta power transformer so that the neutral of the power transformer on the 11 kV side could be solidly grounded. But this also may not be feasible for consideration as the earth fault current is desired to be restricted as stipulated by the manufacturers of the Synch onous machines. It is, therefore, ultimately decided to increase the earth fault current from 300 Amp., as previously proposed, to 1000 Amp., thereby increasing the continuous KVA rating of the transformer from 200 to 660 kVA. Further study made in this matter has revealed that even with 1000 Amp. earth-fault current, high-resistance faults will create a problem in having positive and selective ground relaying. The earth-fault current in this case should at least be 4 times the full-load current for effective ground fault relaying.

The point also arose whether an earthing transformer to be provided should have a short-time rating of one or five minutes. One-minute rating was preferred as there was hardly any justification for having a five-minute rating and thus make the earthing transformer unnecessarily expensive. It was, however, stipulated that

heavy duty is not imposed on the unit or in other words under heavy earth-fault conditions, there shall be no quick cycle of circuit breaker reclosing and fast clearing relays and breakers are used.

The comparative study of continuous kVA rating of the three units, with 300, 1000 and 7000 Amp. respectively, as earth fault-current is shown hereunder. All units are assumed to be meant for one-minute short-time rating.

Continuous kVA rating of earthing transformer with ground current

$$300 \text{ Amp.} = 1900 \times 0.104 \\ = \text{say } 200 \text{ kVA}$$

$$1000 \text{ Amp.} = \frac{11}{\sqrt{3}} \times 1000 \times 0.104 \\ = 660 \text{ kVA}$$

$$7000 \text{ Amp.} = \frac{11}{\sqrt{3}} \times 7000 \times 0.104 \\ = 4020 \text{ kVA}$$

Earthing transformers particularly of zig-zag star type³ are normally designed with 100 per cent impedance based on rated kVA and rated voltage which in the case of earthing transformer is the line-to-line voltage of the system for which the unit is meant.

If Z is the impedance of one phase

ZO is the Zero-sequence impedance of one phase.

$$Z = ZO$$

$$\therefore 100 = \frac{Z \times \text{rated kVA}}{10 \times (11)^2}$$

$$\therefore Z = \frac{100 \times 10 \times (11)^2}{\text{rated kVA}}$$

Rated kVA for 300 Amp. ground current = 1900 kVA

$$\therefore Z = ZO = \frac{100 \times 10 \times (11)^2}{1900} \\ = 63.5 \text{ ohms}$$

Similarly Z for Earthing transformer with 1000 Amp. ground current

$$Z = \frac{100 \times 10 \times (11)^2}{\frac{11}{\sqrt{3}} \times 1000} \\ = 11 \times \sqrt{3} = 19 \text{ ohms}$$

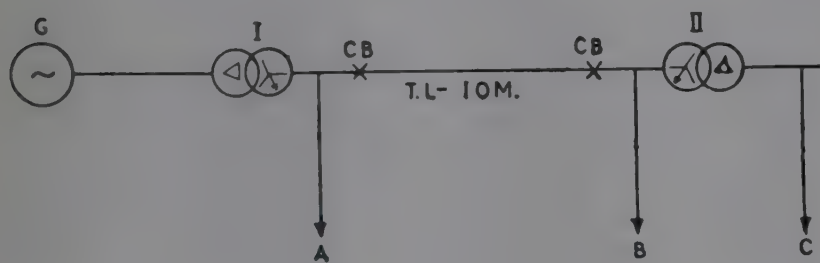
Z for earthing transformer with 7000 Amp. ground current.

$$Z = \frac{100 \times 10 \times (11)^2}{\frac{11}{\sqrt{3}} \times 1000} = 2.73 \text{ ohms}$$

For reactance grounding the reactance could be added in the neutral connection to earth or indirectly by increasing the reactance of the ground return circuit. It may, therefore, be visualized that in the case of earthing transformer with 300 Amp. ground current, the reactance in the ground return circuit is 63.5 ohms per phase. The system will, therefore, be termed as high reactance-grounded system. Similarly, where the reactance in the ground return circuits are 19 and 2.73 ohms, the systems are reactance-grounded and the earthing transformers used will not be effective in stabilising the voltage when single line-to-earth fault occurs.

A system or portion of the system may or may not be effectively grounded depending upon the zero sequence reactance in the ground return circuit.

As an illustration a transmission circuit at random is shown in Fig. 1



	11/132 kV. 31.5 MVA	132/11 kV 31.5 MVA
Transformer	I	II
Generator	$X_1 = 20\%$	$X_1 = 15\%$
	$X_2 = 20\%$	$X_2 = 15\%$
	$X_0 = 5\%$	$X_0 = 15\%$
Transmission line 132 kV 10 miles long		
	$X_1 = 3\%$	
	$X_0 = 10\%$	

At point A three-phase fault current is

$$\frac{100}{35} \times \text{full load current.}$$

$$= 2.85 \times \text{full load current.}$$

At point A single line to earth-fault current

$$\frac{300}{35+35+20} \times \text{full load current}$$

$$= 3.34 \times \text{full load current}$$

$$\text{Ratio } \frac{X_0}{X_1} = \frac{20}{35} = 0.57$$

In this case in case of single line-to-earth fault the line-

to-ground voltage of unfaulted phases is approximately 0.9 times line to neutral voltage⁴.

At point B three phase fault current is

$$\frac{100}{38} \times \text{full load current}$$

$$= 2.63 \times \text{full load current.}$$

At point B single line to earth fault current

$$\frac{100 \times 3}{38 \times 38 + 30} \times \text{full load current}$$

$$= 2.84 \times \text{full load current.}$$

$$\frac{X_0}{X_1} = \frac{30}{38} = 0.79$$

∴ Line to ground voltage of the unfaulted phases comes to approximately 1.05 times line to neutral voltage ($\frac{R_0}{X_1}$ is taken to be 0.1)

At point A, the line-to-earth fault current is more than the three-phase fault current which would mean that the circuit breakers needed would be of higher capacity than those actually required to cater for three-phase fault current. In such cases the single line-to-earth fault current could be brought down and made equal to three-phase fault current with the use of moderate sized neutral reactor. With this small reduction in single line-to-earth fault current, the system will still retain the qualities of effectively-grounded system except that higher neutral insulation would now be called for.

These days high reactance-grounded systems are not commonly erected except where low capacity grounding transformers are employed to create neutral for earthing. This would be a case where the element of expense comes in. For instance, in the case of the power system under study, it would appear that system has all the disadvantages inherent in such a reactance-grounded system.

In Fig. I at point C the system would be ungrounded unless a neutral is created and earthed and for that an earthing transformer of suitable capacity would be needed for effective grounding. All the reactances are taken on 31.5 MVA base.

$$\text{Full load current} = \frac{31.5 \times 1000}{1.732 \times 11}$$

$$= 1660 \text{ Amp.}$$

The three-phase short circuit current at point C

$$= \frac{100}{53} \times \text{full load current}$$

$$= \frac{100}{53} \times 1660 = 3140 \text{ Amp.}$$

It may, therefore, be visualized that it is not an infinite bus at point C, otherwise the three-phase short-circuit current would be

$$\frac{31.5 \times 100}{15 \times 1.732 \times 11} \times 1000 = 11000 \text{ Amp.}$$

The single line-to-earth fault current at point C

$$\begin{aligned} &= \frac{100 \times 3}{53 + 53 + 45} \times \text{full load current} \\ &= 2 \times 1660 = 3320 \text{ Amp.} \end{aligned}$$

For effective grounding, short time kVA rating of the earthing transformer

$$\begin{aligned} &= \frac{11}{\sqrt{3}} \times 3140 \times \frac{3^*}{5} \\ &= 11.92 \text{ MVA.} \end{aligned}$$

Continuous kVA rating of the earthing transformer (assuming 1 minute short-time-rating)

$$= 11.92 \times 0.104 = 1.24 \text{ MVA, say 1.5 MVA}$$

Impedance per phase of the transformer

* 3/5 is a factor which gives equivalent single line-to-earth fault current for effective grounding in terms of 3-phase short circuit current.

$$= \frac{100 \times 10 \times (11)^2}{11920} = 10.1 \text{ ohms}$$

Conclusion

The modern trend is to adopt solidly or effectively grounded systems. The author, therefore, concludes that systems or portions thereof may always be effectively grounded except when certain limitations are imposed on the flow of heavy ground fault currents due to other important factors. In such cases small reactances could be added in the neutral circuits. Effectively grounded systems provide efficient control and protection and selective and positive earth fault relaying. There could be no dangerous transient over-voltages which could result in insulation failures. Solidly or effectively-grounded systems are serving and will serve more efficiently than other modes of grounding.

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[Original mss. received on 7.2.69]

Effect of different sodium polyphosphates has been studied in reducing the viscosity of by-product chalk slurry from an ammonium sulphate plant of Sindri. Appreciable reduction in viscosity by all the four polyphosphate samples has been observed.

Deflocculation of By-Product Chalk Slurry By Sodium Polyphosphates

By RAJENDRA SINGH AND A. K. ROY,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

In the manufacture of ammonium sulphate by the Merseburg process, powdered gypsum is allowed to react with ammonia and carbon dioxide in an aqueous medium to give solid calcium carbonate and ammonium sulphate in solution. The solution is filtered off to give a cake called as "chalk" comprising of calcium carbonate and some unconverted gypsum and impurities originally present in the gypsum. In the Sindri ammonium Sulphate plant, this chalk is repulped with water and the slurry is pumped to an adjacent factory* for the production of cement.

For the transportation of such slurries, studies on viscosity are of considerable importance¹. The present work was undertaken to see the effect of different samples of sodium polyphosphate on the reduction in viscosity of the 'chalk' slurries.

Experimental

Viscosity measurements were made with a Brookfield Synchro-Lectric viscometer model LVT-E, a rotating spindle type viscometer. All the measurements were made at a speed of 30 rpm and with spindle no. 2. Readings were taken immediately after stirring was stopped. The polyphosphates were added to the slurry in the form of solid and after each addition the stirring was continued and the viscosity measured until the lowest value was attained.

For the present studies the chalk sample collected from the secondary filters of ammonium sulphate plant at Sindri was dried at 60°C and ground to pass through a 100 mesh (B.S.) sieve. Slurries of desired consistencies were prepared from the -100 mesh sample so as to obtain homogeneous, reproducible samples of slurry. Analysis of the chalk sample used is given in Table 1. Deflocculating effects of four different sodium polyphosphates have been observed; two of these are commercially available samples and the other two have been prepared by the process developed here.² The pH of 1 per cent solution of the four samples, their P₂O₅ contents and number average molecular weights as determined by titration with caustic soda³ are given in Table 2.

TABLE 1—CHEMICAL ANALYSIS OF THE SECONDARY
FILTER CHALK

Ingredients	% By wt.
SiO ₂ + Insoluble	15.12
R ₂ O ₃	2.22
CaO	43.88
MgO	0.49
SO ₃	3.72
Nitrogen as N	0.23
Loss on Ignition	34.33

* Associated Cements Company Ltd.

TABLE 2— P_2O_5 CONTENT AND NUMBER AVERAGE
MOLECULAR WEIGHT OF THE POLYPHOSPHATES

Sample No.	Polyphosphate	Number Average Mol. wt. (Mn)	P_2O_5 , %	pH of 1% Soln.
1.	Sodium Hexameta-phosphate, (B.D.H.)	680	69	6.5
2.	Sodium Hexameta-phosphate, (Star Chemicals, Bombay)	630	57.6	7.5
3.	Sodium Polyphosphate (from our Pilot Plant, containing 59% Na_2SO_4)	2700	27.0	6.6
4.	Sodium Polyphosphate prepared from commercial grade H_3PO_4	980	69	7.0

60 and 65 per cent w/w slurries of the chalk sample in water were found to be of appropriate consistencies to see the deflocculating effect on it of the polyphosphates. For comparison the deflocculating effect of these polyphosphates on pure calcium carbonate (B.D.H) slurries has also been studied. The results are given in Tables 3 and 4.

Results and Discussion

It is seen from the results given in Tables 3 and 4 that all the four samples with varying number average molecular weights appreciably reduce the apparent viscosity of the pure calcium carbonate as well as of the by-product chalk slurry. Viscosity reduction upto 93 per cent in the by-product chalk and upto 98 per cent in the pure calcium carbonate slurries of the consistencies studied have been observed. The extent of reduction in the apparent viscosity is dependent on the amount of polyphosphate added and finally it comes to a minimum where the value becomes constant. Amount of sample

TABLE 3—DEFLOCCULATION OF SECONDARY FILTER CHALK SLURRY BY SODIUM POLYPHOSPHATES

60% w/w slurry					65% w/w slurry				
Polyphosphate in g. to 150g. slurry	Viscosity in cp at 35°C reduced by				Polyphosphate in g. to 150g. slurry	Viscosity in cp at 35°C reduced by			
	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4		Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
0.0	220	220	220	220	0.0	850	850	850	850
0.1	150	160	200	170	0.2	430	450	560	650
0.2	95	105	175	140	0.4	250	180	410	330
0.3	70	80	150	120	0.6	140	90	320	90
0.4	50	60	125	100	0.8	65	65	180	70
0.5	35	30	90	60	1.0	60	65	130	60
0.6	25	20	65	40	1.2	60	—	130	60
0.8	25	20	50	20	—	—	—	—	—
1.0	—	—	45	20	—	—	—	—	—
1.2	—	—	45	—	—	—	—	—	—
1.4	—	—	—	—	—	—	—	—	—
% Reduction	89	91	80	91	—	93	92.4	84.7	93

TABLE 4—DEFLOCCULATION OF CALCIUM CARBONATE (B.D.H) SLURRY BY SODIUM POLYPHOSPHATE

20% w/w slurry					25% w/w slurry				
Polyphosphate in g. to 100g. slurry	Viscosity in cp at 35°C reduced by				Polyphosphate in g. to 100g. slurry	Viscosity in cp at 35°C reduced by			
	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4		Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
0.0	400	400	400	400	0.0	950	950	950	950
0.1	140	160	150	70	0.1	680	450	540	180
0.2	40	55	105	10	0.2	150	140	400	15
0.3	20	35	50	—	0.3	50	100	250	—
0.4	10	20	35	—	0.4	40	70	150	—
0.5	—	—	20	—	0.5	50	80	110	—
—	—	—	—	—	0.6	—	—	100	—
—	—	—	—	—	0.8	—	—	90	—
—	—	—	—	—	1.0	—	—	90	—
% Reduction	97.5	95	95	97.5		95	92	91	98.5

No. 3 required to bring about the reduction to the same extent as in the case of other samples is more due to the lower percentage of P_2O_5 . One of the polyphosphates developed in this laboratory has been found to be much more effective than other samples in reducing the viscosity of pure calcium carbonate slurry.

Acknowledgement

Thanks are due to Dr. R. M. Bhatnagar, Technologist, for supplying the polyphosphate samples.

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taking about 1 mg. of the ground sample and 300 mg. of potassium bromide (reagent grade, finely ground and previously dried at 400°C) which was intimately mixed by an agate mortar and pestle. This was loaded in a die, evacuated and pressed at 20 tons/sq. inch for nearly 20 min.

The spectra were recorded from 2.5 μ to 18 μ using strip chart recorder at a scanning speed of about 18 minutes for the full range. The spectra of both the samples were qualitatively similar, indicating that the golden brown variety is also biotite. Bands occur at 3440 cm^{-1} (medium broad—OH stretching), 1,625 cm^{-1} (weak—OH bending 1065 cm^{-1} (shoulder), 995 cm^{-1} (very strong, broad—SiO stretching), 680 cm^{-1} (weak broad).

X-Ray Study

X-ray studies of all the three samples were carried out in a Guinear camera, using $\text{CuK}\alpha$ radiation, X-ray data of all these three samples reflect their conspicuous identical nature and show a fairly good agreement with ASTM X-ray diffraction data for biotite (Table 3). However, it may be noted that there are differences in the intensity of the 'd' values particularly on the higher 'd' spacings. It may be due to the differences in radiation, X-ray camera set up used by us and those given in ASTM data. This has been confirmed by obtaining X-ray diffraction data of one of the above samples by Debye Scherrer Technique which shows a much better agreement with the ASTM data. It may be mentioned here that usually the basal lines are most important for the identification of vermiculite in mixtures. Accordingly due consideration was given to the intensity of the lines which are of vital importance for minerals having reflections for vermiculite. It may be said that a basal reflection at about 14 Å should always be more intense than the subsequent low orders if the mineral is a vermiculite⁹. No such line could be found in any of the three samples studied.

Sulphides: The sulphide minerals have been found to be associated with apatite in a particular vein. The following sulphide minerals have been identified:

Pyrite: It is the most common constituent among all the sulphide minerals. Occurs as tabular to wedge shaped crystals within apatite with sharply defined margin. It shows a dull yellowish colour and takes a poor polish, often shows box work pattern; limonitic alternation conspicuous.

Optical Properties

Colour pale yellow; reflectivity very high, isotropic; occasionally shows colloform banding.

Pyrrhotite: Occurs as irregular patches within the fractures of apatite; shows a pale copper red colour; strongly magnetic; takes a good polish.

Optical Properties

The colour is pale creamy pink; strongly anisotropic, showing yellowish brown to dark brown polarisation colours; veins of pyrrhotite within chalcopyrite are not uncommon.

Chalcopyrite: Mostly occurs as large irregular grains and irregular veins within pyrite and apatite, (Fig. 9). The larger grains when observed carefully show fine mesh work of irregular fractures infilled by some materials showing bluish tinge, takes very good polish and shows golden yellow colour.

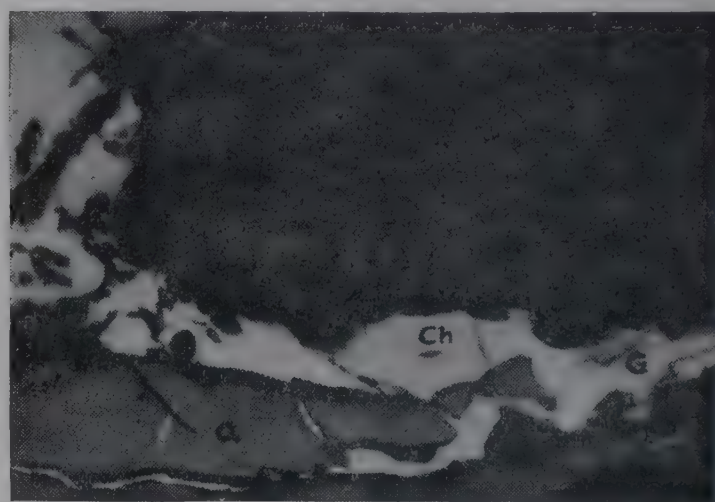


Fig. 9—Chalcopyrite (ch) Veining in Apatite (a)
[Irregular grains of Galena (G) are seen within.]
Oil Immersion $\times$ (960)

Optical Properties

Bright golden yellow in colour; reflectivity high, weak anisotropism in shades of greyish blue colour.

Galena: Its presence with chalcopyrite could be observed only under the ore microscope. It occurs as tiny irregular specks within the chalcopyrite; shows bright white colour and characteristic triangular pits.

Chalcocite/Covellite: Irregular veins composed of fine-grained aggregates of chalcocite and covellite and are frequently found to replace chalcopyrite (Figs. 10 & 11). Covellite is identified easily by its strong reflection, pleochroism from deep blue to pale bluish grey colours and also by its very strong anisotropism, showing fiery red polarisation colour. Chalcocite is pale bluish grey in colour and is weakly anisotropic.

Further work is in progress and will be reported.

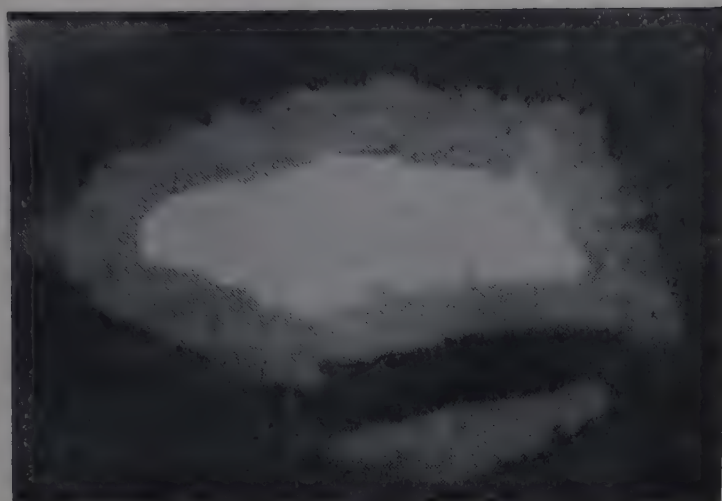


Fig. 10—Rim Replacement of Chalcopyrite (White) by Chalcocite and Covellite (Grey)—Oil Immersion $\times$ (960)

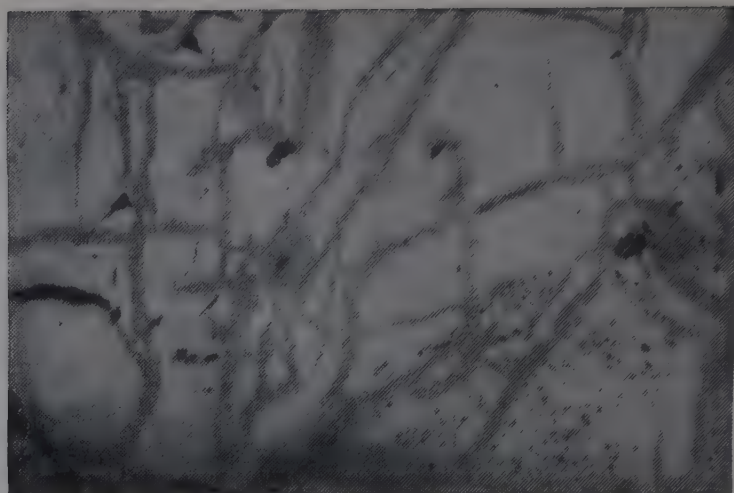


Fig. 11—Veining of Chalcocite and Covellite in Chalcopyrite $\times$ (360)

Acknowledgements

The authors are greatly indebted to Dr. S. Mukherjee of the Geology Department, Calcutta University, for his helpful suggestions, and Dr. S. D. Soman of Bhabha Atomic Research Centre, Trombay, for supplying the rare earth analysis of allanite. The co-operation extended by our colleagues Dr. S. K. Ghosh, Dr. H. C. Roy, Sri A. K. Chakraborty, M. Mishra and S. K. Acharyya, during the x-ray, infrared and DTA studies are also thankfully acknowledged.

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X-ray and conductometric studies on the system urea - mono - and diammonium phosphate prepared under varying conditions have been made. It has been observed that urea does not form adduct with monoammonium or diammonium phosphate in the solid state. In the solution state the existence of a very unstable complex has been found and the instability constants determined are $K_{\text{MAP}} = 1.6 \times 10^{-2}$ and $K_{\text{DAP}} = 1.75 \times 10^{-2}$

Studies on the Urea-Ammonium Phosphate System—Part I

By V. K. SRINIVASA, M. B. MISHRA AND S. K. GHOSH,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Modern trend in the use of high analysis straight and complex fertilizers in preference to the conventional fertilizers, have given rise to the possibility of using urea in place of ammonium nitrate in compound fertilizers, in view of its high plant nutrient content and economy in its production. Hignett, in a recent article¹ has reviewed all available information on the use of urea in compound fertilizers from the view points of chemistry, process technology and the agronomic properties of the products. It has been predicted on the basis of some field tests by T. V. A. that urea-ammonium phosphate will be a very useful fertilizer for rice and its agronomic effectiveness is similar to separate application of urea and ammonium phosphate.

In the dry mixed fertilizer, urea is known to form adduct with $\text{Ca}(\text{H}_2\text{PO}_4)_2$, NH_4Cl and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. But very little is known about urea phosphate system regarding the state of aggregation, nature and mode of formation and stability in the solid or liquid state. It seems that such a study might be helpful for better process and quality control. With this end in view the present investigation was undertaken on the system urea and any source of P_2O_5 such as Mono- and Diammonium phosphate.

Experimental

(i) *Preparation of Samples:* Reagent grades of common fertilizer salts such as urea, mono-ammonium phosphate (MAP), diammonium phosphate (DAP) were used directly from stock bottles. Different grades of high analysis fertilizers have been prepared as follows:

1. Saturated solutions of component salts (urea, MAP or DAP) were mixed in different mole ratios and crystallized at 70-80°C.
2. Stoichiometric mixtures of the component salts (Urea-MAP and Urea-DAP) were repeatedly moistened, ground and dried at 70°C.
3. U-AP1 and U-AP2 were prepared according to Barry² and others³ as follows:

(a) U-AP-1

A slurry having an $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio in the sample 1.32: 1 to 1.35: 1 and a H_2O content of 17-18% was prepared by mixing 85% conc. H_3PO_4 of sp. gr. 1.75 and 25% conc. NH_3 of sp. gr. 0.9 proportionately. The resulting slurry was sprayed on the surface of urea crystals and was thoroughly shaken, with excess of ammonia. The product was dried at 65-70°C in the air oven.

(b) U-AP-2

U-AP-2 was prepared by heating MAP. 26-42 g, urea 12.0 g and H_3PO_4 19.6 g for 2 hrs. at 150°C.

The chemical analyses of the preparations were carried out by the usual methods and are shown in Table 1.

(ii) *Conductometric Measurements:* The titrations were carried out using 0.01M urea, 0.1M MAP and 0.1M DAP solutions and conductivity water was used to prepare these solutions. The measurements were done on a Philips PR 9500 conductivity bridge at 1000 cycles/sec. using a Philips conductivity cell (dip type) PR 9510/00 having a cell constant 1.42. All the measure-

TABLE 1—COMPOSITION OF TYPICAL UREA-AMMONIUM PHOSPHATES PREPARED IN THE LABORATORY

Code	Composition, %					
	N-P ₂ O ₅ -K ₂ O	N	P ₂ O ₅	K ₂ O	Mole. Ratio	Ingredients
U-MAP-1	35-20-0	35.50	20.3	—	4:1	U+MAP
U-MAP-2	24-40-0	24.00	39.96	—	1:1	U+MAP
U-MAP-3	46-20-0	46.6	20.0	—	2:3	U+MAP
U-MAP-4	19-40-0	19.32	49.0	—	1:2	U+MAP
U-DAP-1	37-18-0	37.63	18.74	—	4:1	U+DAP
U-DAP-2	29-37-0	29.17	37.33	—	1:1	U+DAP
U-DAP-3	27-42-0	27.13	42.0	—	2:3	U+DAP
U-DAP-4	26-19-0	25.93	42.90	—	1:2	U+DAP
U-AP-1	42-19-0	42.42	19.60	—	1:3:5	H ₃ PO ₄ +U+NH ₃
U-AP-2	20-46-0	20.23	46.6	—	1:3:3	H ₃ PO ₄ +U+MAP

U—Urea, MAP—Monoammonium Phosphate, DAP—Diammonium Phosphate

ments were made at room temperature and reproducible results were obtained within the limits of experimental error.

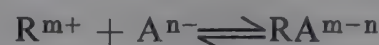
(iii) *X-Ray Analysis*: X-ray diffraction pattern of the samples were recorded in the Guinie camera using Philips X-ray unit PW 1010. CuK α radiation with nickel filter was used, the x-ray tube running at 40 KV and 20 mA. The time of exposure was 5 hr. for each set of samples. The intensities of the lines on the x-ray powder photograph for the phase identification was done by usual method of Hanawalt *et al*⁴.

Results and Discussion

The conductometric data are given in Table 2 and conductometric titration curves are shown in Figs. 1 and 2.

A plot of increasing concentration of monoammonium phosphate (Fig. 1) and diammonium phosphate (Fig. 2) against specific conductance shows clear and detectable breaks at the equivalent points 1:1.72 and 1:1.44 respectively which corresponds to 1:5.16 and 1:4.9 moles. of urea and monoammonium and diammonium phosphate respectively. It is evident from both the curves that after the equivalence point is attained, the specific resistance of the solution becomes almost constant. This indicates that all available urea is used for complexation and the remaining monoammonium phosphate or diammonium phosphate solution gives a constant specific conductance.

The instability constant of the complex was determined according to Yatsimirski. If a complex RA^{m-n} is formed in solution according to the scheme,



Then the instability constant of the complex (K) is given by the equation,

$$K = \frac{(C_R^\circ - a)(C_A^\circ - a)}{a} \quad (1)$$

where C_R[°] and C_A[°] are total initial concentration of the ions R^{m+} and Aⁿ⁻. 'a' is concentration of the complex. Making use of the formula (1), we get the instability constants of the complexes to be

$$(K_{\text{MAP}}) = 1.6 \times 10^{-2}$$

$$\text{and, } (K_{\text{DAP}}) = 1.75 \times 10^{-2}$$

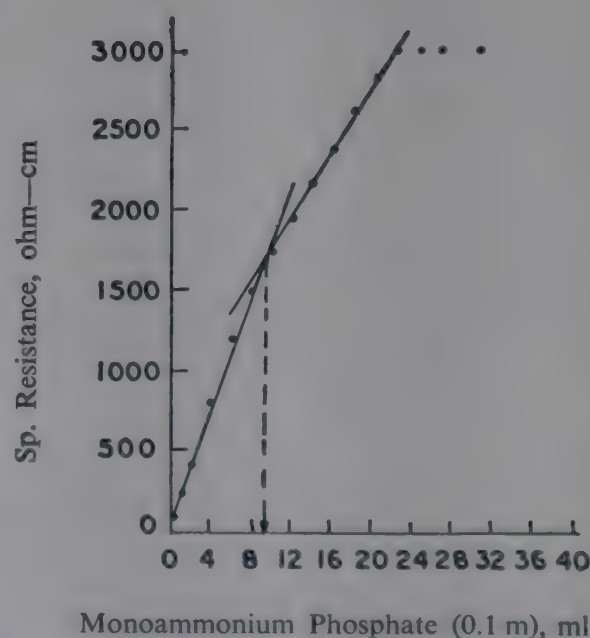


Fig. 1—Conductometric Titration Curves with Increasing Concentration of Monoammonium Phosphate

TABLE 2—CONDUCTOMETRIC DATA

Compound	Initial concentration of urea	Initial concentration of titrant	Stoichiometry	Mole. ratio	Initial conc. complex	K Instability constant
MAP	0.01M	0.1M	1:1.72	1:5.16	0.0085M	1.6×10^{-3}
DAP	0.01M	0.1M	1:1.44	1:4.9	0.0087M	1.75×10^{-3}

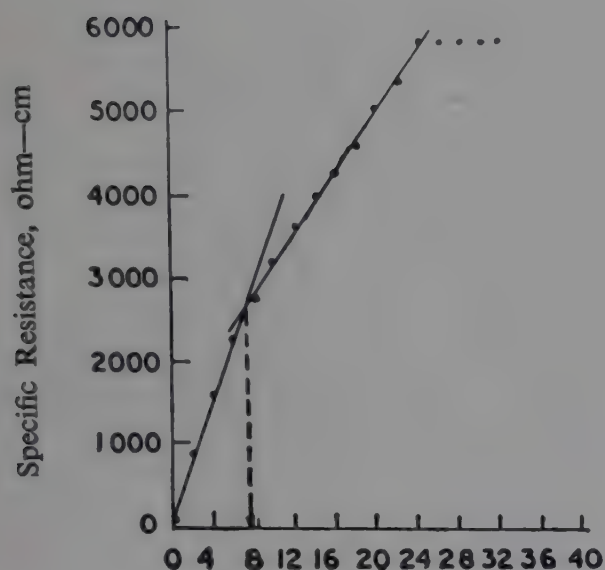


Fig. 2—Conductometric Titration Curves with Increasing Amounts of Diammonium Phosphate

The x-ray diffraction pattern of the stoichiometric mixtures (solid state) of urea-monoammonium phosphate and urea-diammonium phosphate did not reveal any additive compound to formation of urea with mono- or diammonium phosphate. The x-ray diffraction pattern of different variety of combinations of component salts in different mole ratios (shown in Table 1) also did not show any evidence of adduct formation.

X-ray results indicate that urea does not form any additive compound with mono-ammonium phosphate or diammonium phosphate in the solid state although

the presence of the same in the solution state could be detected from conductivity measurements. The low instability constants (Table 2) indicate that the complex as one very unstable in the solution state and the conductometric measurements reveal that urea can form a stable complex only if the system has instability constants in the higher order.

Indorovakaya and Mergolis⁶ from the Solidus-Liquidus isotherm of the system urea, NH_4NO_3 , H_2O and $\text{NH}_4\text{H}_2\text{PO}_4$ or $(\text{NH}_4)_2\text{HPO}_4$ have observed that in the solution state urea forms adduct with $\text{NH}_4\text{H}_2\text{PO}_4$ or $(\text{NH}_4)_2\text{HPO}_4$ but not in the solid state. This observation corroborates our result reported here.

Acknowledgement

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A comparative morphological and anatomical study was made with two varieties of diploid and tetraploid grapes. Morphologically, tetraploids showed many diagnostic features like vigorous growth, thick and deep green leaves with increased leaf area and serrations, short and stout internodes, thick petioles and tendrils. The U-shape character of petiolar sinus was observed in some leaves of both diploids and tetraploids. The leaf, petiole, stem and tendril were thicker in tetraploids and the difference between diploid and tetraploid parts was found to be statistically significant. The increase in cell size of cortical cells, vascular bundles and pith tissue indicated complete tetraploidy.

Studies on Some Morphological and Anatomical Characteristics of Induced Tetraploid Grapes (*Vitis Vinifera* L.)*

By P. K. DAS,

*Planning & Development Division,
Fertilizer Corporation of India, Ltd., Sindri, Bihar*

In the present investigation some morphological and anatomical studies were undertaken in two varieties of grape, viz. Pusa Seedless and Bharat Early, out of the colchiploidy induced in eleven varieties¹, in order to get a comparative idea of diploids and tetraploids.

Materials and Methods

The data were recorded in diploid and tetraploid materials of Pusa Seedless and Bharat Early from ten representative plants of each. The plant parts were sampled from similar positions and at the same developmental stage. For anatomical studies transverse sections of stem, leaf, petiole and tendril of both diploids and tetraploids were made with paraffin method, after fixing in FAA for 24 hr. and then storing in 70 per cent alcohol. Sections of 8-10 microns were cut and stained with safranin and light green and finally mounted in canada balsam.

Observations

MORPHOLOGICAL CHARACTERISTICS;

(i) *Habit of Growth*—Tetraploid twigs in general showed greater growth and vigour both under pot

and field conditions as compared to the corresponding diploids. Thicker and stouter internodes, petioles, tendrils, thicker and dark green leaves with prominent veins and more leaf area with more number of serrations (dentations) at the margin were noticed in both the varieties. Pusa Seedless was comparatively more vigorous in growth than Bharat Early. The data recorded on the extension growth of one year old plants are presented in Table 1.

(ii) *Vine Characters*—It is apparent that internode in tetraploids decreased by 11.24 and 19.18 per cent in Bharat Early and Pusa Seedless respectively, and the difference was found to be statistically significant. In respect of internode thickness, tetraploids registered 29.16 and 45.66 per cent increase in Bharat Early and Pusa Seedless respectively and the difference between diploid and tetraploid was significant at 5 per cent level in both the cases.

(iii) *Tendril Characters*—The tendrils in tetraploid shoots were conspicuously thicker than the diploids. The percentage increases of thickness of tendrils in tetraploids were 34.45 and 42.85 in Bharat Early and Pusa Seedless respectively. The difference with the corresponding diploids is statistically significant at 1 per cent level.

* The investigation was undertaken while the author was working in the Division of Horticulture, Indian Agricultural Research Institute, New Delhi.

TABLE 1—EXTENSION, GROWTH AND VINE CHARACTERS OF TWO VARIETIES OF DIPLOID AND TETRAPLOID GRAPES

Variety	Ploidy	Growth, Cm.	Aver. Inter-node Length, cm.	Decrease over 2n, %	't' value	Aver. Inter node Thickness, cm.	Increase over 2n, %	't' Value
Bharat Early	2n	166.9	4.36	11.24	4.16**	0.384	29.16	14.71**
	4n	186.6	3.87	—	—	0.496	—	—
Pusa Seedless	2n	184.7	5.22	19.18	4.72	0.519	45.66	13.83**
	4n	212.7	4.38	—	—	0.756	—	—

* Significant at 5% level

** Significant at 1% level

TABLE 2—LEAF SIZE, SHAPE, SERRATION AND THICKNESS OF DIPLOID AND TETRAPLOID GRAPES

Variety	Ploidy	Aver. Leaf Area, sq. cm.	In-crease over 2n, %	't' value	W/L ratio (shape)	In-crease over 2n, %	't' value	Aver. Serration Number	In-crease over 2n, %	't' value	Aver. Leaf Thickness, micron	In-crease over 2n, %	't' value
Bharat Early	2n	66.35	16.20	2.41*	1.40	4.29	0.33	41.94	28.71	9.05**	100.80	43.40	16.37**
	4n	77.10	—	—	1.46	—	—	53.98	—	—	144.55	—	—
Pusa Seedless	2n	90.70	25.71	7.64**	1.16	9.49	2.90*	63.67	18.30	3.95**	105.35	42.21	20.23**
	4n	114.02	—	—	1.27	—	—	75.32	—	—	149.85	—	—

* Significant at 5% level

** Significant at 1% level

(iv) *Leaf Characters*—The leaf area increased with the increase in ploidy level, more in Pusa Seedless than in Bharat Early. The difference between diploid and tetraploid leaves was significant at 1 per cent level in Pusa Seedless and at 5 per cent in Bharat Early. So far as the leaf form (width/length) is concerned, tetraploid leaves were broader than the length, i.e. greater W/L ratio, in both the varieties; statistically significant at 5 per cent level only in Pusa Seedless.

With the decrease of petiole length by tetraploidy, the P/L (petiole/length of mid vein) ratio also decreased in both the varieties. Nevertheless, the difference of petiole length of diploids and tetraploids was statistically significant. The petiole thickness increased significantly due to tetraploidy—22.16 per cent in Bharat Early and 34.09 per cent in Pusa Seedless.

The number of serrations increased due to tetraploidy, more in Bharat Early than in Pusa Seedless and the difference between diploids and tetraploids was significant at 1 per cent level. Leaf thickness also increased significantly due to tetraploidy 43.40 per cent in Bharat Early and 42.21 per cent in Pusa Seedless (Table 2).

Anatomical Studies

Data on transverse sections of stem, petiole, tendril and leaf could not be statistically analysed since the samples on which measurements were based had been obtained from a limited number of materials.

It would, however, be apparent from Table 3 that the size of the cells in stem right from the epidermis to the pith increased by chromosome doubling in both the varieties. The length and breadth of the single layer of rectangular epidermal cells also increased.

The vascular bundles, which are conjoint and collateral, increased in size by tetraploidy. Similarly, the cell size of the pith increased, as is evident from the reduction in their number in tetraploids in unit area. For instance, tetraploid Bharat Early had on an average 40.1 cells as against 59.9 in diploid and the corresponding figures for Pusa Seedless were 40.8 and 63.2.

The cells of petiole also increased in size from the periphery to the centre of petiole. The epidermis, which consisted of a single layer of rectangular cells, increased in both length and breadth. In contrast to stem bundles, the vascular bundles in petiole were conspicuously

developed. Due to the doubling of somatic chromosome complement the size of such vascular tissue increased in both the cases. The size of pith tissue also increased (Table 4).

The cells of the tendrils also increased with the increase in the chromosome number. In both the varieties, the size of epidermal cells, vascular tissue and pith cells increased in tetraploid forms as compared to their corresponding diploids (Table 5).

Discussion

Induced tetraploids, in their vegetative phase of growth, showed many striking variations from their diploid progenitors, which formed good indices in early stages of growth in grape for isolating tetraploid branches. Tetraploids of both the varieties were vigorous growers than their diploid counterparts. However, most of the induced polyploid fruit plants, excepting *Anona*, have been recorded to be slow growing^{3,4, 6-8}. Islam⁵,

TABLE 3—ANATOMICAL FEATURES OF DIPLOID AND TETRAPLOID STEM

Variety	Ploidy	Epidermal cell, micron		Vascular bundle, micron		Number of Pith cells in Unit Area
		Length	Breadth	Length	Breadth	
Bharat Early	2n	8.3	7.0	179.1	75.9	59.9
	4n	13.1	11.2	261.5	151.4	40.1
Pusa Seedless	2n	9.8	7.7	189.0	80.5	63.3
	4n	14.7	11.9	273.0	150.5	40.8

TABLE 4—ANATOMICAL FEATURES OF DIPLOID AND TETRAPLOID PETIOLE

Variety	Ploidy	Epidermal cell, micron		Vascular bundle, micron		Number of Pith cells in Unit Area
		Length	Breadth	Length	Breadth	
Bharat Early	2n	8.5	6.5	152.5	98.1	42.1
	4n	13.1	8.5	241.3	180.0	25.9
Pusa Seedless	2n	9.1	7.0	161.0	108.0	45.8
	4n	14.0	9.1	252.0	182.0	27.4

TABLE 5—ANATOMICAL FEATURES OF DIPLOID AND TETRAPLOID TENDRIL

Variety	Ploidy	Epidermal cell, micron		Vascular bundle, micron		Number of Pith cells in Unit Area
		Length	Breadth	Length	Breadth	
Bharat Early	2n	10.1	6.8	81.1	58.9	111.1
	4n	11.2	7.9	125.1	67.9	73.2
Pusa Seedless	2n	11.2	7.0	87.5	63.7	104.4
	4n	12.6	8.0	149.1	65.1	74.4

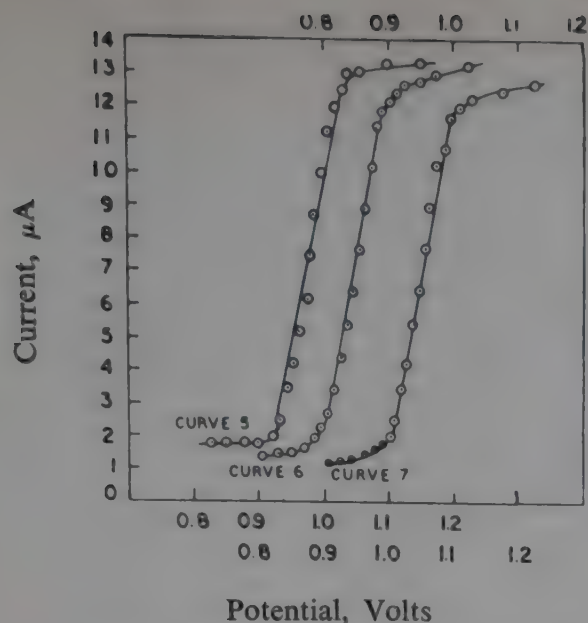


Fig. 3—Polarograms of Cd^{2+} ($2.98 \times 10^{-3}\text{M}$) in Increasing Concentrations of Biuret

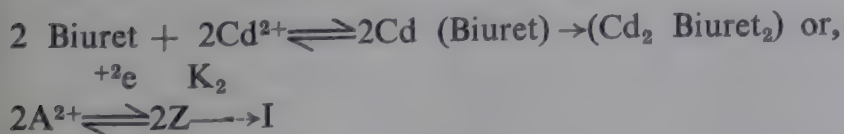
Curve 5—Conc. of Biuret 5.79×10^{-3}
 Curve 6—Conc. of Biuret 9.72×10^{-3}
 Curve 7—Conc. of Biuret 1.33×10^{-2}

TABLE 2—POLAROGRAMS OF Cd^{2+} IN INCREASING CONCENTRATIONS OF BIURET

$[(\text{Cd}^{2+}) = 2.98 \times 10^{-3}\text{M}]$

Concentration of Biuret Added	$E_{1/2}$, volt	Shift	$i_d, \mu\text{A}$	Sensitivity
0.0	-0.975	0.000	10.50	1/100
5.79×10^{-3}	-0.970	+0.005	10.25	„
9.72×10^{-3}	-0.965	+0.005	10.00	„
1.33×10^{-2}	-0.963	+0.002	9.25	„
1.66×10^{-2}	-0.962	+0.001	9.00	„

However, i_d is observed to decrease regularly with increasing concentrations of biuret. According to Vlcek¹⁰, the shift towards more positive potentials may be due to (i) non-complexation, or (ii) dimerization of the product of electrode reaction and subsequent inactivation. However, in case of a non-complexing media, i_d remains constant and $E_{1/2}$ shifts towards more positive potentials. Whereas, in case of dimerization of the electrode reaction proper and its becoming inactive subsequently, the i_d decreases but $E_{1/2}$ shifts towards more positive potentials. In such a case, the following reaction⁴ takes place:



where A is the depolarizer (biuret in this case), Z is the product of electrode reaction and I is the inactive product

of dimerization reaction. Polarographic currents controlled by the rate of diffusion and by the rate of the chemical reaction inactivating the product of a reversible electrode process have been observed during the anodic oxidation of several ene-diolic substances⁶⁻⁸, and during the reaction of manganous ions⁵, mercuric ion complex⁹ with DTA.

Recently, an anodic oxidation of cadmium amalgam⁷, in a buffered solution containing EDTA, has been reported. The current (in this case) is given by

$$\bar{i} = nF \cdot 10^3 \bar{q} \frac{D[Z]}{\mu} \quad (\text{II}),$$

$$\text{where } \mu = \sqrt{D/K_2[Z]} \quad (\text{III}),$$

where, $\bar{i}$ is mean current, $\bar{q}$ is mean surface area of the depolarizer, μ is thickness of the reaction layer, $[Z]$ is the product of the electrode process.

Simultaneously, the diffusion condition for depolarizer A is valid

$$\bar{i} = \bar{i}_d - \bar{K}[A_a] \quad (\text{IV})$$

The ratio $[A]_o / [Z]_o$ is given by the Nernst equation

$$\frac{[A]_o}{[Z]} = P^* = \text{Exp} \left[\frac{nF}{RT} (E - E^\circ) \right] \quad (\text{V})$$

where, E° denotes the standard reduction potential $\dagger$ for the redox couple

$$P^* = \left(\frac{CK_2 t_1}{1.51} \right)^{1/3} \cdot \frac{\bar{i} - \frac{\bar{i}}{\bar{i}_d}}{(\bar{i}/\bar{i}_d)^{2/3}} \quad (\text{VI})$$

where C is the depolarizer concentration, and t_1 the drop time. Hence, the corresponding equation for the wave can be expressed as follows:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\bar{i}^{2/3}}{\bar{i}_d - \bar{i}} + \frac{RT}{3nF} \ln \frac{CK_2 t_1}{1.51} \quad (\text{VII})$$

and for the half-wave potential

$$E_{1/2} = E^\circ - 0.36 \frac{RT}{nF} + \frac{RT}{3nF} \ln CK_2 t_1 \quad (\text{VIII})$$

which shows that the half-wave potential depends on

$\dagger$ If the reduction product does not form an amalgam¹¹ with mercury, the half-wave potential is virtually identical with standard redox potential, E_o .

drop-time, on the rate constant for inactivation and on depolarizer concentration.

In the present case, the value of K_2 comes out 9.1×10^{-3} which proves conclusively that the complexation reaction of cadmium and biuret is much slower than the inactivation reaction of its products.

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This paper describes the occurrence of a basic copper phosphate (provisionally identified as cornetite), allanite and a few sulphidic minerals, hitherto unknown in this area. Detailed mineralogical studies of all these minerals along with those described earlier have been carried out with optical microscope, x-ray, infra-red, differential thermal, thermogravimetric and spectroscopic methods.

Investigations on the Mineralogy of the Apatite Veins Occurring in the Area around Kasipatnam, Visakhapatnam District, Andhra Pradesh

By R CHOUDHURI AND K. C. BANERJI,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

The area under consideration covers a small tract of Eastern Ghats, consisting predominantly of khondalite, leptynite, pyroxene granulite and pyroxene gneiss, (containing both orthopyroxene and clinopyroxene) granite and pegmatite of precambrian basement complex.

The occurrence of apatite-magnetite-biotite/vermiculite-bearing veins with occasional association of zircon has already been reported¹⁻⁵. The mineralogical aspects

of apatite and zircon have also been discussed in considerable details⁶⁻⁷. In the present paper the occurrence and mineralogical characters of allanite and some sulphidic minerals like pyrite, chalcopyrite, pyrrhotite, chalcocite, covellite and galena have been described. An uncommon green mineral—suspected to be a basic copper-phosphate—has also been reported. All these minerals occur in association with an apatite vein in Sitampeta area near Kasipatnam village. Some new data on the physical and

optical properties of the already described minerals have also been incorporated in this paper.

Most of the apatite veins along with those minerals mentioned above, are restricted strictly to a preferred set of joints trending approximately NW-SE and having a steep (75°) South-Western dip.

The veins usually occur as lenses ranging in length from a few feet to 500 feet. The thickness of these veins also vary considerably from an inch to 8 feet (at the thickest portion of the lens). The lenses are arranged in an en-echelon pattern. In many cases, major veins have been found to be accompanied and running parallel by minor veins. Swelling and pinching phenomenon of these veins at a depth is not an uncommon feature. Considerable number of these veins show zonal arrangement (both symmetrical and asymmetrical type). These zones are represented by quartzofelspathic bands, biotite/vermiculite-bands and green pyroxene bands (Salite). All these three bands are found to occur together and also mutually exclusive of each other.

Mineralogy

The apatite-bearing veins show considerable amount of variation in respect of their mineral assemblage, and from this point of view they can be divided into two broad groups. In one, the apatite biotite/vermiculite and magnetite bearing veins are intimately associated with pink coloured K-feldspar and quartz; consequently they are ascribed as apatite or magnetite bearing pegmatite veins, depending on the predominance of apatite, magnetite or biotite/vermiculite. All these four minerals may occur together or independently. In the other type, quartzofelspathic minerals are practically absent, thereby rendering the veins economically more potential. Sometimes the late cherty material infills the interspaces of the apatite crystals belonging to the veins of second category.

The mineral association of these veins could be described in terms of mainly four phases, namely the phosphate, oxide, silicate and sulphide of which the sulphide group of minerals are restricted only to one vein. Following mineral assemblages have been found in the apatite bearing veins of the present area:

1. Apatite	}	Phosphate group
2. Basic copper phosphate		
3. Magnetite	}	Oxide group
4. Ilmenite		
5. Martite		
6. Spinel (hercynite)		

7. Biotite/vermiculite	}	Silicate group
8. Salite		
9. Allanite		
10. Zircon		
11. Pyrite	}	Sulphide group
12. Chalcopyrite		
13. Pyrrhotite		
14. Chalcocite		
15. Covellite		
16. Galena		
and		
17. Malachite (Disseminated)		Carbonate group (insignificant)

Phosphate (Apatite)

It occurs either as perfectly crystalline (Fig. 1) or massive bodies. Sometimes the crystals are arranged in criss-cross fashion with void interspaces (Fig. 2). The optical, x-ray and infra-red studies carried out by the authors⁶ revealed it to be predominantly a fluorapatite. DTA studies of the pure washed sample of apatite carried out subsequently also showed an almost featureless curve, characteristic of fluorapatite. Unwashed sample of apatite however shows two endothermic peaks at about 130°C and 540°C and one exothermic peak at about 900°C (Fig. 3). These peaks are similar to those of illite which might have partially filled up the void interspaces of the apatite in appreciable amount. Spectroscopic investigation reveals presence of copper and nickel in traces.



Fig. 1—Big Apatite Crystals Showing Twinning



Fig. 2—Apatite Crystals Arranged in Crisscross Fashion with Void Interspaces

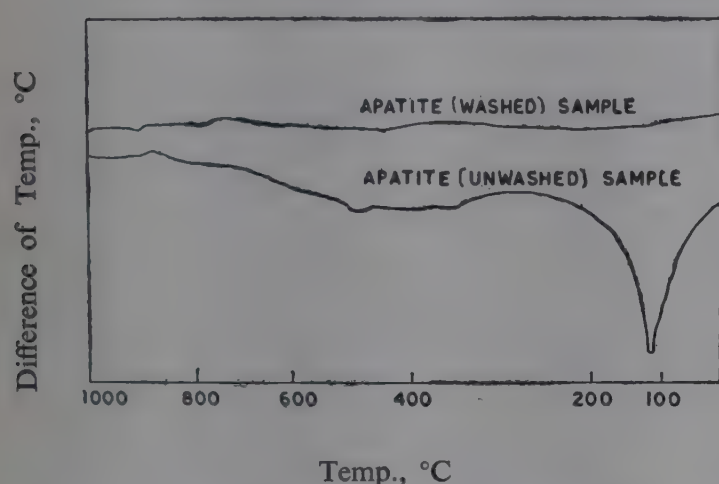


Fig. 3—DTA Curves of Washed & Unwashed Apatites

(Basic Copper Phosphate)

This mineral is found to occur in association with apatite in very small amount. It occurs as tabular or platy form showing colour zoning with light green at the margin and dark bottle green near the core. The mineral is flanked by a very thin layer of cherty material. Under the microscope the green patches are found to be dispersed unevenly and occasionally as veins within the grains showing feeble anisotropy. It sometimes shows colloform banding. The grains of these minerals show slight variation in their refractive indices, depending on the intensity of their colour. Of the 150 grains observed, some 120 grains show n in the range between 1.695 and 1.700 while for the rest it fluctuates between 1.700 and 1.705. An x-ray diffraction analysis, (Table 1) carried out to identify the greenish fraction favours the most probable association of cornetite, a basic copper phosphate, with fluorapatite. For a true identification a partial analysis of the sample was also attempted polarographically with a view to determine its copper content which indicated its value in the order 0.49% only, much

TABLE 1—X-RAY DATA OF CORNETITE AND APATITE

Kasipatnam Apatite & Cornetite		ASTM Data for Cornetite		ASTM Data for Apatite	
dÅ	I	dÅ	I	dÅ	I
—	—	5.48	—	—	—
—	—	5.07	—	—	—
—	—	4.56	—	—	—
—	—	4.29	—	—	—
—	—	3.68	—	—	—
—	—	3.53	—	—	—
3.48	w	—	—	3.44	20
3.35	vvw	—	—	—	—
3.198	w	3.17	80	—	—
—	—	—	—	3.11	8
—	—	—	—	3.08	30
3.05	w(b)	3.04	100	—	—
2.98	w	2.95	50	—	—
2.80	s	—	—	2.80	100
2.78	w	—	—	2.78	40
2.75	vw	2.74	30	—	—
2.70	ms	—	—	2.71	60
2.64	w	—	—	2.63	30
—	—	2.54	30	2.53	5
—	—	—	—	2.49	5
—	—	2.44	30	—	—
2.29	vvw	—	—	2.30	5
—	—	—	—	2.26	20
—	—	—	—	2.14	10
2.05	vvw	2.06	70	2.06	10
2.01	vvw	—	—	2.00	5
1.93	vw	—	—	1.94	40
1.88	vw	1.897	10	1.89	10
1.84	vw	1.833	5	1.84	60
1.795	vvw	1.791	20	1.80	30
1.767	vvw	—	—	1.77	30
—	—	1.74	20	1.75	30
1.73	vvw	—	—	1.72	30
1.63	vvw	—	—	1.64	10
1.60	vvw	—	—	1.61	10
—	—	1.57	40	—	—
—	—	1.545	40	1.54	5
—	—	1.509	30	—	—
1.46	vvw	1.471	10	1.47	20
1.45	vvw	—	—	—	—
1.44	vvw	—	—	—	—

w = Weak, vw = Very Weak, vvw = Very Very Weak, s = Strong, ms = Medium Strong, b = Broad.

below the concentration of copper usually found in pure cornetite. However, the extent to which such analysis of samples taken from a specimen scooped out of a fraction which is so highly dispersed is questionable. On account of this, and because of the dissimilarity of the optical behaviour of this mineral with those of

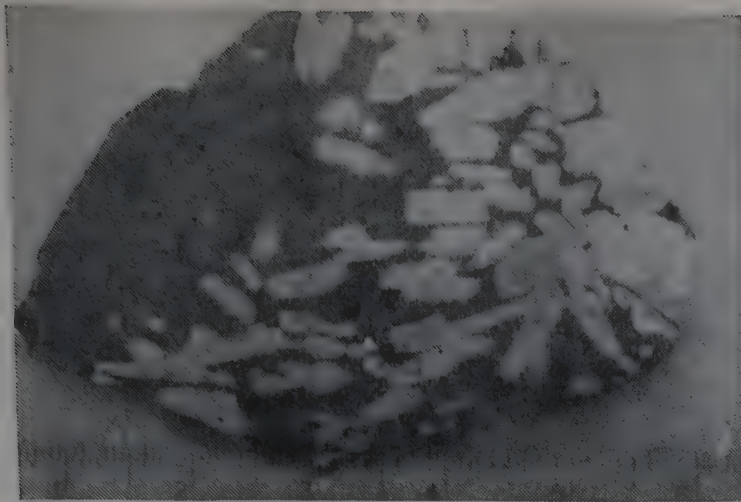


Fig. 4—Apatite Crystal Showing Intimate Association with Magnetite

cornetite the X-ray evidence for its identification as cornetite can, at best, be kept as provisional.

Oxides

Magnetite: It occurs in intimate association with apatite (Fig. 4) and biotite. The occurrence and mineralogy of these magnetite deposits have already been reported by Sriramdas⁴. The present authors want to record the following findings.

Under the ore microscope magnetite shows numerous ex-solution intergrowth of spinel exsolved along (100) planes of the host. Sometimes spinel shows wavy nature in their arrangement indicating post ex-solution deformation. Magnetite in many cases is highly fractured and intensely martitised along these fracture planes. The martite needles are elongated parallel to their 0001 direction which show broadening phenomena ultimately leaving relics of magnetite islands in martite indicating progressive oxidation of magnetite. Lucoxenic alteration of magnetite is also seen.

Ilmenite is also present. It shows dark brown colour and low reflectivity and occurs mostly as laths along the octahedral planes within magnetite. Sometimes lath shaped ilmenite has been found to be bordered by small specks of spinel, the elongation of the latter is distinctly at an angle to that of the former and parallel to the cubic planes of the host. It may be mentioned here that the ilmenite is completely devoid of ex-solution intergrowths of hematite, a feature indicative of low oxidation potential of the source melt.

Spectroscopic examination of this magnetite shows presence of nickel and copper in traces.

Zircon: Good crystals of zircon sometimes as long as 10 cm containing automorphic crystals (Fig. 5) or cast of apatite have been found in some of the apatite veins.

Their mode of occurrence and mineralogy have already been discussed earlier⁷.

Silicates

Allanite: This mineral has been found to be closely associated with apatite occurring as small pockets. It occurs in massive form, showing greyish black colour and resinous lustre and is highly brittle in nature. The specific gravity of the mineral varies from 3.52 to 3.60.

Under the microscope it shows moderately strong pleochroism with X = light brown, Y = reddish brown and Z = greenish brown, $Z > Y > X$; N_x was found to be $1.744 \pm .002$, $N_y = 1.750 \pm .002$ and $N_z = 1.752 \pm .002$. The birefringence appears to be quite low indicating it to be a heterogeneous mixture of unaltered and altered materials.

The allanite sample was analysed for total rare earths which was found to be 21.5 per cent (total rare earth and thorium oxide). Lange gives the chemical formula and approximate composition of allanite as:



Approximate composition (%): Ce 51, Y 8 and thoria 3.5

X-ray study of this mineral also supports the above observation. The X-ray data is given in Table 2. X-ray diffraction patterns were obtained in a Debye-Scherrer camera of 114.6 mm diam., and a filtered $CuK\alpha$ radiation was employed with X-ray tube running at 40 KV and 20 MA and exposure for 8 hrs. It is apparent from the optical and X-ray data that the allanite is composed, in a large part, of metamict mineral.

Salite: This mineral essentially occurs either as pure bands or as a constituent of the gneissic rock cut across by the apatite pegmatite veins. Salite is

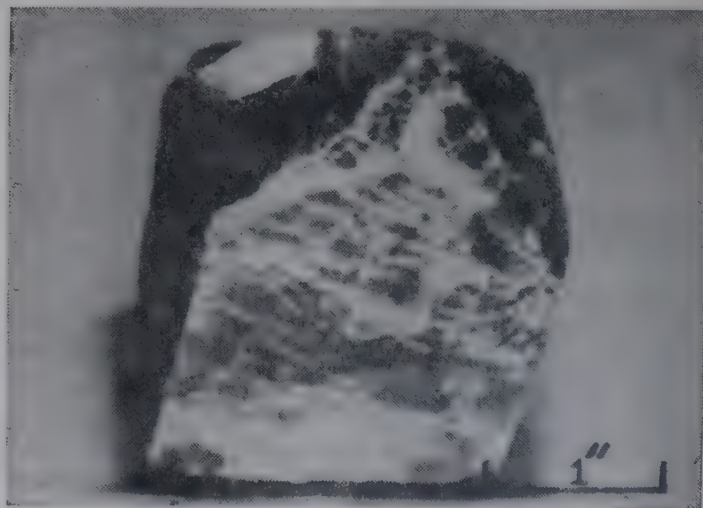


Fig. 5—Zircon Crystal Containing Automorphic Apatite (White)

TABLE 2—X-RAY DATA OF ALLANITE

Kasipatnam Allanite		ASTM data for Allanite metamict		ASTM data for Allanite non-metamict	
dÅ	I/I ₁	dÅ	I/I ₁	dÅ	I/I ₁
—	—	9.30	30	—	—
—	—	—	—	9.20	20
—	—	—	—	8.05	20
—	—	—	—	7.96	20
—	—	—	—	5.09	10
—	—	5.07	30	—	—
—	—	—	—	5.01	10
—	—	4.84	10	4.87	6
—	—	4.67	10	4.69	20
—	—	4.62	50	—	—
—	—	4.43 b	3	—	—
—	—	4.10	3	—	—
—	—	4.00	20	—	—
—	—	3.81 b	10	—	—
—	—	—	—	3.78	10
—	—	3.60 b	1	3.59	10
3.48	w	3.50	80	3.52	40
—	—	3.34	30	—	—
—	—	—	—	3.30	10
3.26	vw	3.27	20	—	—
—	—	3.20	10	2.23	10
—	—	2.96	100	—	—
2.93	s	—	—	2.92	100
—	—	—	—	2.91	100
—	—	—	—	2.86	50
—	—	2.83	30	2.82	10
2.77	ms	2.79 b	3	—	—
—	—	2.74	30	—	—
2.68	vw	2.67	80	2.68	40
2.615	ms	2.60	40	2.62	40
2.549	vw	2.54	30	—	—
—	—	—	—	2.51	20
—	—	—	—	2.50 b	10
—	—	2.48 b	3	—	—
2.416	vw	2.43	30	—	—
—	—	2.40 b	3	—	—
—	—	2.33 b	10	2.33 b	10
—	—	2.24 b	10	—	—
—	—	2.20 b	10	2.20	20
2.144	vw b	2.16	30	2.14	10
—	—	2.13 b	30	2.10 b	4
—	—	2.06 b	10	2.05 b	10
1.90	vw	1.90 b	20	1.91 b	4
—	—	—	—	1.89 b	20
—	—	—	—	1.78 b	4
—	—	—	—	1.67 b	10
1.652	w	1.65 b	30	1.65 b	10
—	—	1.63 b	60	1.64 b	20
—	—	—	—	1.56 b	20
—	—	1.47 vb	10	—	—
—	—	1.42	20	—	—
—	—	—	—	1.12 b	4

s = strong, ms = medium strong, w = weak, vw = very weak,
b = broad vb = very broad.

restricted to the gneiss only near its contact with the above mentioned veins. Fresh specimens of this mineral show dark green colour, while the altered variety shows yellowish green colour. One set of parting parallel to 001 is conspicuous. The specific gravity of this mineral is 3.02. Under the microscope, the mineral shows weak pleochroism. $N_y = 1.710$, $\pm .002$, $2V_z = 57$, $ZAC = 43^\circ$.

Biotite: Dark, dark brown and brown mica books have been generally found to be developed along the outer margin of the apatite veins, and also as a constituent of the apatite bearing pegmatite veins. The large sheets of mica occasionally measure 2 feet across (Fig. 6) and their thickness sometimes ranges upto 3/4 feet. The mineralogical characteristics of these mica had been described by Betaraya and Abde Ali under the heading of "Kasipatnam Vermiculite".

The present authors have carried out detail physical studies of these micas and observe that they are predominantly biotite. The physical investigation incorporates determination of refractive indices of these minerals under polarizing microscope, differential thermal analysis, thermogravimetric analysis, ion-exchange capacity, X-ray and infrared studies. Three types of representative samples based on their colour difference were studied which include dark bronze mica (No. 1), dark brown mica (No.2) and golden brown mica (No. 3). It may be pointed out that all these micas have essentially dark bronze colour which due to weathering action give dark brown to bronze colours. Thin interlaminae of cherty materials are frequently met with.

Optical Studies

The n_y of the three samples were determined using sodium Monochromator.

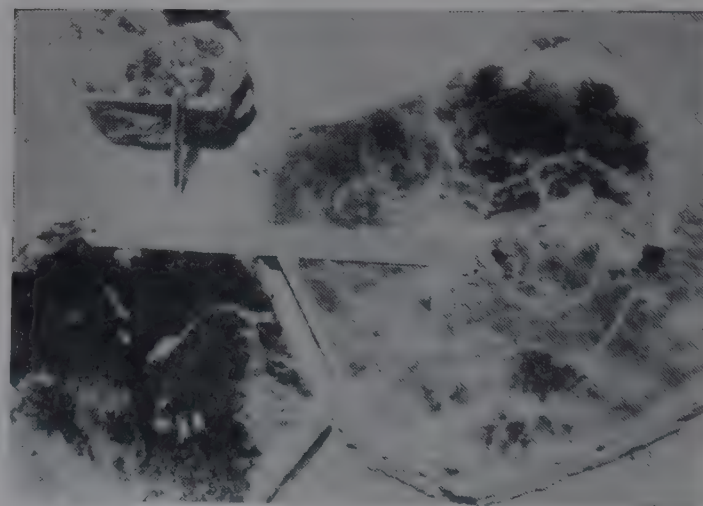


Fig. 6—Large Sheets of Biotite Showing Colour Zonation

No. 1	No. 2	No. 3
$n_y = 1.664 \pm 602$	1.662 ± 002	1.662 ± 002

Thus all the three samples appear to have almost identical R.I. and point to their biotitic nature.

The DTA was performed in a fully automatic Linseis apparatus using platinum foil sample holders and ignited alumina as reference material. The thermocouple used was Pt-Pt/Rh (13 per cent) and heated at a rate of 10°C/min. No. 1 variety shows almost featureless curve without having any peak (Fig. 7). It may be mentioned here that there is no peak upto 100°C in the thermogram of biotite, Hence it may be inferred that the sample No. 1 consists of biotite mica. Samples No. 2 and 3 (Fig. 7) however show some very weak peak temperatures ($\pm 5^\circ\text{C}$) which are given below:

No. 2	No. 3
100°C 250°C very diffused	100°C—medium bulge
550—very weak, broad bulge	100°C—weak bulge
700—weak bulge	500°C } diffused bulge
	600°C }
	690°C }

From these DTA curves it appears that there may be an insignificant association of vermiculite/illite in these micas. To examine the diffused bulges over 500°C in details, the dehydration behaviour of these two samples had been investigated by thermogravimetric analysis (Fig. 8) which was performed in atmospheric pressure and at a room temperature of 27°C using platinum cup as sample holder. The heating rate was maintained at 10°C/min. The characteristic decomposition steps with corresponding per cent water loss were as follows:

No. 2	No. 3
100°C-400°C 3.5% (gradual water loss)	100°C-460°C 4.3% (gradual water loss)
400°C-430°C 1% water loss	480°C-500°C 0.5% water loss
550°C-600°C 0.5% water loss	580°C-600°C 0.7% water loss
	680°C-700°C 0.5% water loss

It is known that both illite and vermiculite show a considerable water loss at about 100°C. It is also established that in case of vermiculite, the water loss is in three steps, below 100°C, from 250°C to 400°C and from 600°C to 850°C. Illite shows a gradual water loss in between 100-350°C and a relatively large loss of (OH)

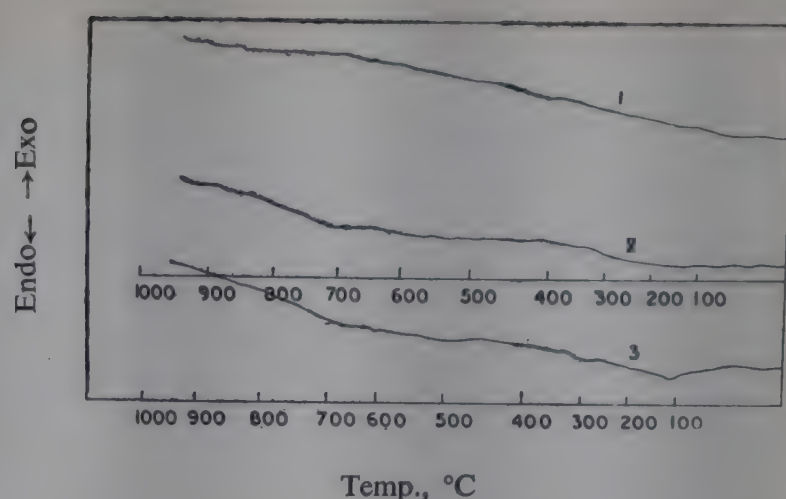


Fig. 7—DTA Curves for Showing Biotite Samples, 1, 2 & 3

lattice water from 350°C to about 600°C. It will be evident from the thermograms that there is a gradual water loss in both the cases from 100°C onwards, a feature indicative of the presence of illite, but the water loss in the range of 680°C-700°C in sample No. 3 is an added indication of the presence of very small proportion of vermiculite and/or illite. The base exchange property of this sample shows a very low value of 4.98 m.e./100g. It is known that base exchange value of vermiculite is between 120-140 and that of illite between 20-40 me. Thus, it is evident that the value obtained in sample No. 3, though falls far short of the value of either of these two minerals, is relatively much closer to illite than vermiculite.

The total water loss of sample No. 1 which has a dark colour is 4.84 per cent whereas the water loss of the other two samples having dark bronze and brown colour is 6 per cent. Hence it appears that even an increment of approximately 1 per cent water may be one of the contributing factors for the change in the colouration properties of biotite.

Infrared spectra for the samples Nos. 1 and 3 were studied in the solid phase by potassium bromide disc technique using the Perkin Elmer dual grating spectrophotometer, model 421. KBr pellets were prepared by

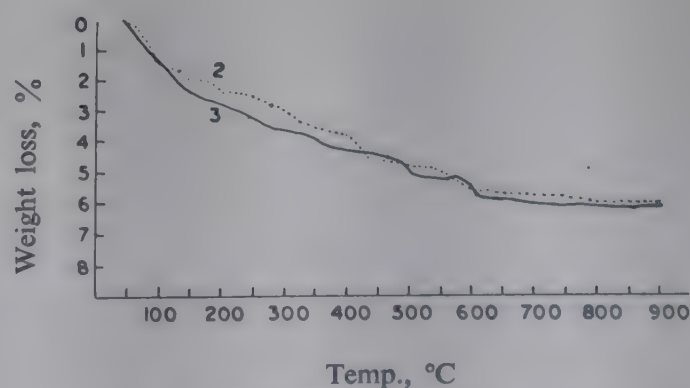


Fig. 8—TGA Curve for Biotite Samples 2 & 3

TABLE 3—X-RAY DATA OF BIOTITE SAMPLES

No. 1		No. 2		No. 3		Biotite ASTM-2-0045		Vermiculite ASTM-16-613		Illite ASTM-9-334	
dÅ	I/I ₁	dÅ	I/I ₁	dÅ	I/I ₁	dÅ	I/I ₁	dÅ	I/I ₁	dÅ	I/I ₁
—	—	—	—	—	—	—	—	14.2	100	—	—
10.1	mw	10.1	w	10.1	w	10.1	100	—	—	9.9	80
—	—	—	—	—	—	—	—	17.14	15	—	—
—	—	—	—	—	—	—	—	4.76	10	4.9	60
4.60	vw	4.60	vw	4.60	vw	4.59	20	4.57	60	—	—
—	—	—	—	—	—	—	—	—	—	4.46	100
—	—	—	—	—	—	—	—	4.41	10	—	—
—	—	—	—	4.2	vvw	—	—	4.35 b	10	4.29	40
—	—	—	—	—	—	—	—	4.25	—	—	—
—	—	—	—	—	—	—	—	—	—	4.11	40
3.95	vvw	3.95	vvw	3.93	vvw	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	3.88	60
3.80	vvw	—	—	3.80	vvw	—	—	—	—	—	—
3.68	vvw	3.68	vvw	3.68	vvw	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	3.65	50
3.53	vvw	—	—	3.53	vvw	—	—	3.56	25	—	—
3.37	vw	3.37	vw	3.365	vvw	3.37	100	—	—	3.36	100
3.30	vvw	—	—	3.28	vvw	—	—	—	—	—	—
3.15	vvw	—	—	—	—	3.16	20	—	—	3.10	50 b
3.02	vvw	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	2.92	20	2.85	30	2.86	60 b
2.66	vw	2.66	vw	2.65	w	2.66	80	—	—	—	—
2.635	s	2.63	s	2.63	s	—	—	2.615	50	—	—
—	—	—	—	—	—	—	—	2.570	50	2.570	100
2.52	vvw	2.50	vvw	2.51	vvw	2.52	40	2.525	45	—	—
2.45	m	2.44	m	2.44	m	2.45	80	2.43	5	2.45	50
—	—	—	—	—	—	—	—	—	—	2.39	60
—	—	—	—	—	—	—	—	2.380	—	—	—
2.31	vw	2.30	vw	2.30	vw	—	—	2.365	35 b	—	—
2.27	vw	2.27	vvw	2.26	vvw	2.28	20	2.265	5	—	—
—	—	—	—	—	—	—	—	—	—	2.24	50
2.18	mw	2.18	w	2.17	w	2.18	80	2.20	5 b	—	—
—	—	—	—	—	—	—	—	2.17	—	—	—
—	—	—	—	—	—	—	—	—	—	2.14	60
2.0	vvw	2.0	vvw	2.0	vvw	2.0	80	2.080	5 b	—	—
—	—	—	—	—	—	—	—	2.047	—	1.992	60
—	—	—	—	—	—	—	—	2.01	10 b	—	—
—	—	—	—	—	—	—	—	1.975	—	1.94	40
—	—	—	—	—	—	1.91	20	—	—	—	—
—	—	—	—	—	—	—	—	1.82	5 b	—	—
—	—	—	—	—	—	—	—	1.79	—	—	—
1.75	vvw	1.74	vvw	1.74	vvw	1.75	20	1.725	10 b	—	—
—	—	—	—	—	—	—	—	1.715	—	—	—
1.68	vw	1.68	vvw	1.67	vvw	1.67	80	1.695	5	—	—
—	—	—	—	—	—	—	—	1.665	15	1.650	60 b
1.542	ms	1.542	ms	1.54	ms	1.54	80 b	1.543	10	—	—
1.525	w	1.52	vw	1.52	vw	—	—	1.528	70	—	—
—	—	—	—	—	—	—	—	1.514	25	—	—
—	—	—	—	—	—	—	—	1.502	15	1.500	—
—	—	—	—	—	—	1.47	20	—	—	—	—
—	—	—	—	—	—	1.43	20	—	—	—	—
—	—	—	—	—	—	1.36	60	—	—	1.345	50
1.335	w	1.33	w	1.33	w	1.33	40	—	—	—	—
1.315	vvw	1.315	vvw	—	—	1.315	40	—	—	—	—
1.305	vvw	1.305	vvw	1.30	vvw	—	—	—	—	1.297	60
1.28	vvw	1.28	vvw	1.275	vvw	—	—	—	—	1.269	40
—	—	—	—	—	—	—	—	—	—	1.245	50

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EDITOR: S. N. ROYE

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Nuclear methods are gaining importance for the determination of soil density and moisture content. The applicability of gamma ray absorption in soils for the bulk density determination in the laboratory has been investigated using a NaI (Tl) scintillation spectrometer. Also, the variation in transmission of gamma rays through soils is studied with the variation in moisture content.

Laboratory Determination of Soil Density Using Gamma Ray Attenuation

By B. S. SASTRY, W. SETHURAMAN, K. APPALACHARYULU,
OM SHEEL AND K. C. BANERJI,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

Recently, the use of absorption and back-scattering properties of gamma rays for the determination of soil density and moisture content is gaining much importance. Several authors¹⁻⁶ have indicated the possibility of developing a nuclear densitometer. The advantage of nuclear methods over the conventional ones for the determination of bulk density of soils accrues mainly from the following facts: (a) rapid results because of short time required for sampling in the field, (b) comparatively higher accuracy, and (c) minimum soil disturbance in the field measurements.

The scattering of gamma radiation within the soil or its transmission through the soil is a function of its bulk density. Methods based on the former are comparatively less accurate and require strong sources. The transmission technique has, therefore, been preferred for the measurement of bulk density of soils. Of course, in the application of this method, a stringent requirement is that all scattered radiation should be avoided in order to ensure the validity of exponential-inverse square law for gamma ray attenuation in soils. In this paper, a systematic investigation has been carried out in the laboratory to assess the applicability of the technique for soil density measurements, so that a suitable modification of the apparatus later makes it convenient for field work.

Theoretical

The principle of the method is that a beam of gamma

rays from a nearly point-source is transmitted through the soil, and only the primary radiation is measured. The theory for gauges based on this principle has been worked out earlier^{4,5}. In this case, as already pointed out, the attenuation follows the relation

$$I_x = I_0 \exp [-(\mu/\rho) \times \rho] \quad (1)$$

where I_0 and I_x are the radiation intensities before and after transmission through a soil sample of thickness x and μ/ρ is the mass absorption co-efficient of soil, ρ being its wet bulk density. Thus, a plot between $\log I$ (count rate) and wet bulk density, ρ , should result in a straight line. The attenuation, as is well known, is due to the interaction of gamma rays with the soil particles. The interaction process may be mainly Compton scattering for the energy of the radiation under consideration (Cs^{137}), though to a very small extent, photoelectric process may also contribute. Any way, the relative contributions cannot be estimated easily and hence only the total attenuation coefficient is taken into account. The value of μ/ρ for sandy soils⁵ has been taken as $0.077 \text{ cm}^2/\text{g}$. This value also includes the average effect due to the presence of water. In the strict sense the equation governing the attenuation is of the form,

$$I_x = I_0 \exp [-(\mu/\rho)_s \times \rho_s + \mu_w \theta] \quad (2)$$

where I_0 and I_x are same as before, $(\mu/\rho)_s$ is the mass absorption co-efficient for oven dry soil, ρ_s is dry bulk density of the soil, μ_w is the mass absorption co-efficient of water and θ is the volumetric moisture content.

The reported values⁴ for mass absorption co-efficient

are $0.071 \text{ cm}^3/\text{g.}$ for sandy soil, $0.066 \text{ cm}^3/\text{g.}$ for clay soil and $0.086 \text{ cm}^3/\text{g.}$ for water. Adopting these values, the dry bulk densities ρ_s for soil samples used have been calculated theoretically from the above equation. Then, the wet bulk densities $\rho_{w.d}$ are deduced with the aid of the expression,

$$\rho_{w.d} = \rho_s + \rho_w \quad (3)$$

Here, ρ_w is the bulk density of water and is given by

$$\rho_w = d_w V_w/V_s \quad (4),$$

where d_w = density of water approximately equal to 1

V_w = volume of water, and

V_s = volume of soil.

Converting the volume of water present in the soil into percentage of water by weight

$$\frac{\text{Percentage of water content by weight}}{100} = \frac{d_w V_w}{\rho_s V_s}$$

$$\text{i.e., } \frac{d_w V_w}{V_s} = \frac{\rho_s (\text{Percentage of water content by weight})}{100}$$

$$\therefore \rho_{w.d} = \rho_s \left(1 + \frac{\text{Percentage of water content by weight}}{100} \right) \quad (5)$$

Experimental

The block diagram (Fig. 1) shows the schematic arrangement of the apparatus used. The electronic set-up consisted of a single crystal scintillation spectrometer with a $2.5 \text{ cm} \times 2.5 \text{ cm}$ NaI (Tl) crystal optically coupled to a RCA 6199 phototube. The output from the anode of the phototube was fed to a cathode follower and the output of which, in turn, was connected to a non-overloading linear amplifier. The output pulses from the amplifier were sorted out according to the energies by a single channel analyser and then finally counted by a decade scaler operated in conjunction with a timer. The best possible resolution obtained for the above spectrometer at an interdynode potential of 75 V was 10 per cent for the 0.661 Mev gamma rays from Cesium-137. The system had been extensively checked for reproducibility and the peak shift observed in this case was less than 0.5 per cent over a period of 8 hr.

The radio-active source, a $20\mu\text{C}$ Cs^{137} solution in the chloride form, was deposited in a 2 mm. diam. drilled

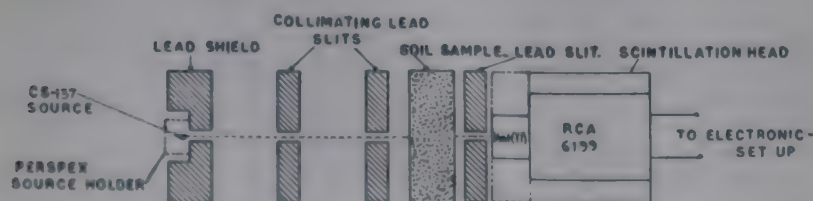


Fig. 1—Block Diagram of the Experimental Arrangement

groove, provided in a perspex holder. The uniformity of source spreading was achieved by placing initially in the groove insulin diluted to 1:3 with water. The solution was then dried under an i.r. lamp and then covered by an aluminium foil of thickness 3 mg/cm^2 to avoid any contamination. The source holder was mounted in a lead block of dimensions $10 \text{ cm.} \times 5 \text{ cm.} \times 2 \text{ cm.}$ with a central hole of 3 mm. diam. to allow the direct radiation to pass through. Two more lead slits were placed between the source and the detector to collimate the radiations from the source.

The soil samples in which the attenuation was studied were of dimensions $50 \text{ mm.} \times 50 \text{ mm.} \times 25 \text{ mm.}$ and were positioned very near the detector. Thus, the arrangement ensured that the detector saw mostly the primary radiation. The soil samples used in this work were prepared in a standard compaction mortar to a compaction equal to 7500 ft. lbs. of work done in three equal steps. With the experimental arrangement described above, the direct as well as transmitted differential spectra have been first recorded in order to ascertain whether the attenuation of gamma rays in soils follows an exponential relation as shown in Fig. 2. In this case, the source to detector distance was kept fixed at 25 cm. to effect good collimation. It can be seen that the shape of the spectrum was preserved with only a reduction in the intensity.

Next, the effect of distance on the counting rate in soils of two different bulk densities was studied. The distances employed between the source and the detector ranged from 2 to 20 cm. The primary peak count rate in each case corrected for the inverse square effect

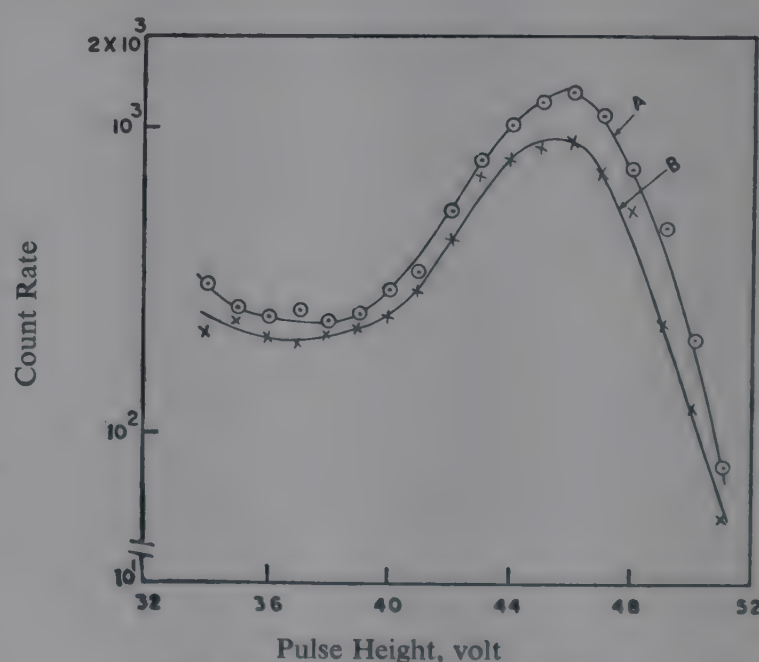


Fig. 2— Cs^{137} Differential Spectrum
A—Energy Distribution in Air
B—Energy Distribution in Soil

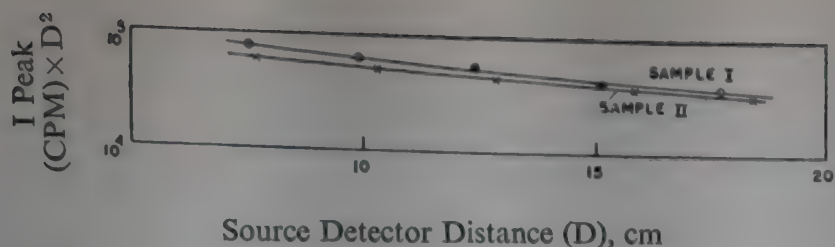


Fig. 3—Primary Count Rate against Source Detector Distance

of the distance when plotted on a semilog paper against source-detector distance showed a linear relation (Fig. 3). Thus, from these observations it was clear that the exponential inverse square relation is valid for soils of different kinds. In other words, the nature of absorption of gamma rays in soils being known, this variation can be conveniently used for determining bulk densities of soil samples.

In order to determine the bulk density of soils using the exponential attenuation of gamma rays, the following procedure was adopted. The soil samples of different composition and moisture contents were prepared as described earlier and their wet bulk densities noted gravimetrically. Arranging the source and detector in an exactly reproducible geometry, the count rate in air was determined. Then, the soil samples were inserted individually and the corresponding count rates at the primary peak were recorded in a channel of 75 KeV. In all these cases, the counting times were adjusted to obtain 10,000 counts or more to ensure a statistical error of 1 per cent. In the present work some four to seven numbers of soil samples were taken in four sets of observation for densities ranging from 1.6 to 2.3 g./c.c. These samples consisted of sandy soil from Barauni (Bihar), sandy soil and sandy silt from Sindri (Bihar), and bentonite clay from Barauni. The measurements were repeated several times and the averages were taken. For each set a linear calibration graph was obtained by plotting the log count rate versus $\rho_{w.d}$ (Gravi.). These are shown in Figs. 4 and 5. From these calibration plots

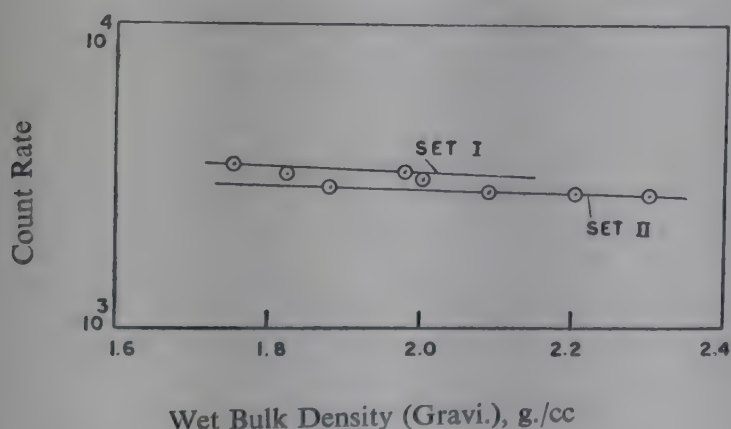


Fig. 4—Calibration Graph

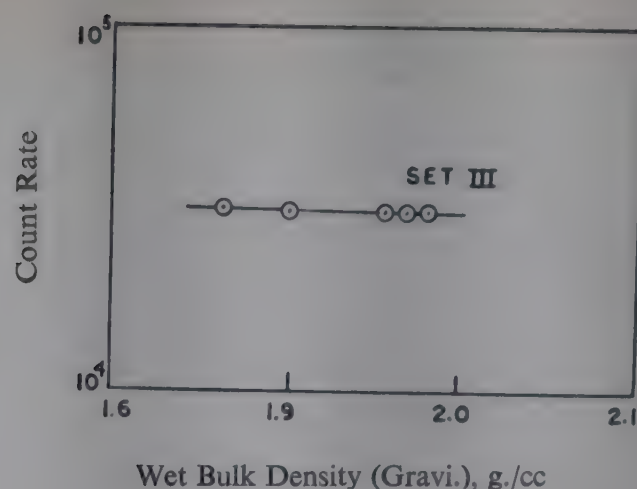


Fig. 5A—Calibration Graph

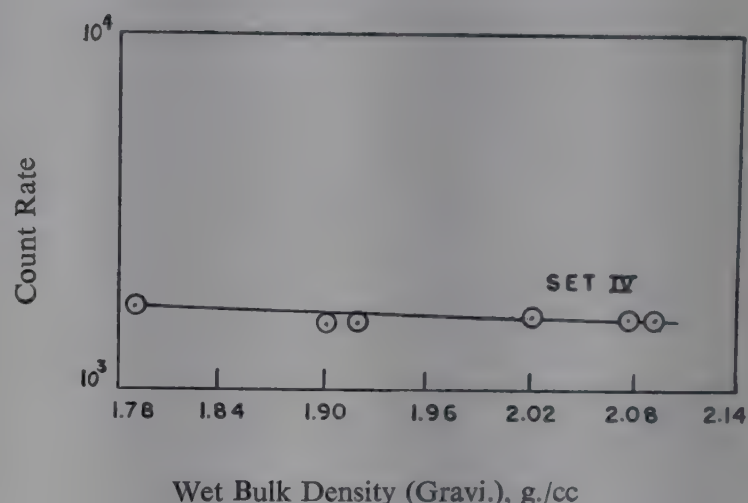


Fig. 5B—Calibration Graph

the wet bulk density of any unknown sample in that range can be determined directly. Later, by constructing a suitable sealed standard density model the count rate can always be maintained to a constant value by a slight adjustment of the voltage of the detector. Thus, the calibration can always be checked easily before applying the instrument for unknown density measurements.

Alternatively, in the absence of a standard sample, the density values can also be computed as described in the previous section if the type of soil is known. The theoretically computed values from the observed count rates in various cases are shown in Table 1 together with the values obtained gravimetrically for comparison. From this table it can be inferred that the nuclear method yields substantially accurate values for the wet bulk densities. The experimental inaccuracies in this case led to an overall estimated error of 5 per cent.

The effect of moisture content of the soils on bulk density and thereby on the transmission count rate was also investigated. The variation in moisture content varies the wet bulk density and hence the count rate. For this,

TABLE 1

Set No.		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
I	ρ w.d. computed in g./c.c.	1.64 Sandy soil (7.5%)	1.87 Sandy soil (10%)	1.88 Sandy soil (12.5%)	2.10 Sandy soil (15%)	—	—	—
	ρ gravimetric g./c.c.	1.75	1.82	1.98	2.00	—	—	—
II	ρ comp.	1.83 Sandy soil (15%)	1.94 Sandy silt (12.5%)	2.09 Sandy soil (14%)	2.11 Sandy soil (15%)	—	—	—
	ρ gravi.	1.88	2.09	2.20	2.30	—	—	—
III	ρ comp.	1.76 75% Sandy soil + 25% Bentonite clay (12.5%)	1.96 85% soil + 15% clay (15%)	1.87 90% soil + 10% clay (15%)	1.87 90% soil + 10% clay (20%)	1.78 90% soil + 10% clay (25%)	—	—
	ρ gravi.	1.91	1.97	1.96	1.98	1.86	—	—
IV	ρ comp.	1.63 Sandy silt (5%)	1.93 Sandy silt (7.5%)	1.97 Sandy silt (10%)	2.11 Sandy silt (12.5%)	2.14 Sandy silt (15%)	1.96 Sandy silt (17.5%)	2.10 Sandy silt (20%)
	ρ gravi.	1.79	1.90	2.02	2.09	2.08	2.02	1.92

NOTE: The figures in parentheses indicate moisture content.

moisture contents ranging from 5 to 20 per cent had been used in sandy silt samples. The count rate versus moisture content is shown in Fig. 6.

As expected with the increase in moisture content upto 14 per cent the bulk density increased and consequently the count rate decreased owing to the increase in attenuation. Beyond 14 per cent moisture content, the bulk density decreased and hence attenuation also decreased upto 17 per cent. But at 20 per cent moisture content though the bulk density was decreased, the attenuation increased instead of decreasing which may be observed from the above figure. This may be attributed to an increase in the effective atomic number⁵ of the soil sample due to more water content which compensates for the decrease in density, resulting in the observed increase in attenuation. On the other hand, for samples of low bulk density with less water content, the attenuation is less than in the previous case due to the

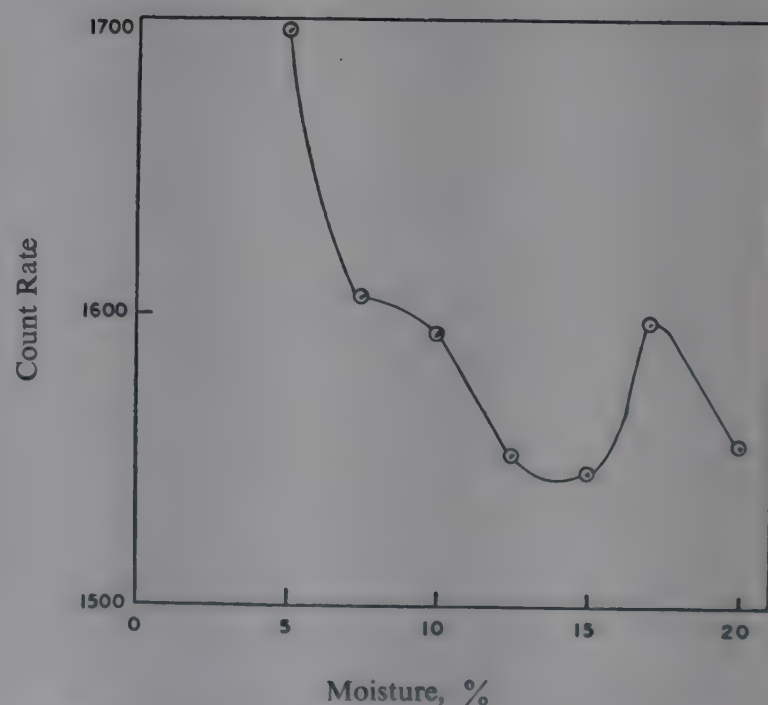


Fig. 6—Count Rate Vs. Percentage Moisture Content

existing air spaces in the sample, i.e. low effective atomic number.

Conclusion

Though the computational procedure is time-consuming in determining the wet bulk densities, the calibration method yields quite accurate results in a short time. However, the former method does not require a standard sample. Further, miniaturization of the equipment makes this method suitable for direct field measurement of soil bulk densities. Alternatively, the moisture content can be directly deduced, if the bulk density is known from a calibration plot wet bulk density versus volumetric moisture content.

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A process has been developed for the concentration of phosphorus in the form of ferrophosphorus to the extent of 56.5 per cent as P_2O_5 from low grade iron-rich phosphatic rocks and converting this into water-soluble phosphatic fertilizers. Ferrophosphorus is prepared by heating these rocks with additives like mica and limestone at $1300^\circ C$. Water-soluble phosphatic fertilizers can be obtained from this ferrophosphorus by dissolving it in a mixture of hydrochloric and nitric acids and subsequent removal of the iron salt by ether extraction.

A New Process for the Preparation of Water-soluble Phosphatic Fertilizers from Iron-rich Phosphatic Rocks

By H. ROY, S. K. ADHYA AND S. K. SHARMA,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

Iron-rich phosphatic rocks are not considered as economic raw materials for the preparation of phosphatic fertilizers by the conventional process. This is because of the fact that on acidulation, soluble iron salts, when neutralized with ammonia, are precipitated as $FePO_4$ which is neither water nor citrate-soluble and is there-

fore rendered unutilizable as a fertilizer. Although solvent extraction method has been successfully utilized from the acidulated rock phosphate solution to remove some of the major impurities such as calcium chloride or nitrate, the removal of iron salt from the product without loss of equivalent phosphate has so far proved unsuccessful commercially.¹⁻⁵

Again, low grade phosphate rocks are upgraded by a beneficiation process. But beneficiation does not remove iron to an appreciable extent from the iron-rich phosphatic ores⁶. To get rid of iron salts from such rocks, a procedure has been reported in which the acid solution is treated with additional quantity of iron salt to precipitate all phosphate as ferric phosphate. This is then chlorinated at an elevated temperature (550-750°C) in presence of a reducing agent when oxy-chloride of phosphorus is formed and separated from iron salts¹¹. The process seems to be uneconomical. Moreover, in the case of low grade phosphate rocks where P₂O₅ content cannot be upgraded to the desired level, in spite of beneficiation such a process is likely to consume large quantities of mineral acid for acidulation. It is, therefore, desirable that the phosphorus in the rock sample should be concentrated prior to the acidulation and separation in order to make the process economical. A concentration of phosphorus by a thermal treatment and removal of the major portion of the other constituents of such rock phosphates (in the form of slag) seems to be a promising step in making phosphatic fertilizers. Ferrophosphorus rich in phosphorus can be prepared on heating iron oxide with rock phosphates and other fluxing agents in a reducing condition⁶. The formation of ferrophosphorus is possible because the iron oxides are easily reduced and the distribution co-efficient of phosphorus is much higher for the iron than the slag phase in the molten condition⁷. Further problem lies in its final winning in the form of iron-free phosphoric acid or a phosphatic fertilizer. In order to achieve this, an examination of both the chemical dissolution as well as the roasting method is of utmost importance. So far no attempt has been made in this direction. In the present investigation, attempts have, therefore, been made to prepare ferrophosphorus from iron-rich phosphatic rocks by thermal treatment and to see if separation of soluble salts from acidulated ferrophosphorus is possible by solvent extraction for making iron-free water-soluble N-P fertilizers.

Experimental

600 parts of an iron-rich phosphatic rock, crushed to sizes 2-5 mm. average diam., and 200 parts of each of limestone and mica of the same size were mixed and taken in a pot made of magnesite brick, lined with a thin layer of coke dust. The chemical composition of the ingredients is given in Table 1.

The pot containing the mixture was heated to 1300°C in a carbon resistance furnace when a molten mass was formed. This molten state was maintained for one hour

TABLE 1—COMPOSITION OF RAW MATERIALS, % BY WT.

Constituents	Iron-rich Rock Phosphate	Mica Dust	Limestone
P ₂ O ₅	15.70	—	—
CaO	20.68	—	51.3
SiO ₂	29.46	43.87	6.2
Al ₂ O ₃	12.14	36.00	
Fe ₂ O ₃	15.93	2.28	
MgO	2.81	0.53	
K ₂ O	—	9.78	
Na ₂ O	—	0.86	—
TiO ₂	—	0.24	—
CO ₂	—	—	42.40
F	0.84	—	—
Cl	1.37	—	—
Loss on Ignition	—	7.15	—
	98.93	100.71	—

inside the furnace. During the whole furnace operation, the atmosphere was found reducing with carbon monoxide. The molten mass was then quenched in air. On solidification, the mass separated into two phases—a greyish glassy mass and a metallic iron mass. The chemical composition of these two phases is shown in Table 2. The whole mass was then crushed to 2-5 mm. sizes and was separated by a small magnet. The fused product was about 80 per cent of the ingredients used and the iron mass separated was 15 per cent of the total fused mass. The phosphorus content of the iron mass was found to be 56.5 per cent (as P₂O₅).

In order to see whether the phosphorus of ferrophosphorus can be converted into phosphatic fertilizers, the

TABLE 2—COMPOSITION OF THE THERMALLY-TREATED PRODUCT, % BY WT.

Constituents	Glassy Mass	Iron Lump
P ₂ O ₅	3.00	56.5
Fe	Trace	76.0
Fe ₂ O ₃	Trace	Trace
CaO	32.30	Trace
SiO ₂	37.50	Trace
Al ₂ O ₃	20.60	—
TiO ₂	Trace	Trace
K ₂ O	2.57	—
Na ₂ O	0.23	—
MgO	2.40	—
	98.60	—

TABLE 3—ANALYSIS OF THE FINISHED PRODUCT
(WATER-SOLUBLE N-P FERTILIZER)

Constituents	% by wt.
P ₂ O ₅	52.6
NH ₃	27.25
Cl as (NH ₄)Cl	5.0
Fe ₂ O ₃	0.5

sample was dissolved in a mixture of hydrochloric and nitric acids. The proportion of nitric acid was so adjusted just to effect complete oxidation of ferrous to ferric chloride and phosphorus to phosphoric acid. Ether was effectively used to remove the ferric chloride from the solution after adjusting its hydrochloric acid concentration to 6 molar. The residual hydrochloric acid was then removed from the iron-free solution by distillation. A completely water-soluble granular product was obtained by neutralization with ammonia and subsequent crystallization of the resultant solution. Its composition is given in Table 3. The determination of P₂O₅ of the final product was carried out by the method developed by Kumar *et al*⁸ and other constituents by the conventional methods.

Results and Discussion

Table 1 shows that the phosphatic rock sample contains 15.93 per cent ferric oxide and 15.7 per cent P₂O₅. The iron compound in this rock exists as goethite⁹. Above 400°C goethite decomposes to ferric oxide which is reduced easily at higher temperature in the region of 1300°C by carbon monoxide. During reduction, the apatite constituent of the ore also undergoes reaction with the other ingredients containing fluxing constituents, like potash, lime and silica, and a slag consisting of K₂O-CaO-SiO₂-Al₂O₃ is easily formed and remains in a fluid condition. It is known that the distribution co-efficient of phosphorus is much higher for iron than for the slag phase in the molten condition⁷. The formation of ferro-phosphorus thus continues until the metal is saturated. It is evident from the result that maximum phosphorus that can be taken up by molten iron is 24.66 per cent (56.5 per cent as P₂O₅, Table 2).

The glassy slag contains only 3 per cent P₂O₅. It is interesting to mention here that 90 per cent of this

P₂O₅ is citrate-soluble. It was previously observed⁹ by us that thermally treated iron-rich rock phosphates with mica additive yields α -Ca₃(PO₄)₂ which is citrate soluble⁹. Here also perhaps this constituent crystallizes out from the melt.

Acid dissolution of ferrophosphorus is facilitated by the formation of phosphoric acid and ferric chloride only. It is known that ferric chloride and hydrochloric acid form a solvated complex H (FeCl₄). This complex is soluble in ether¹⁰. We have observed that ether can separate quantitatively ferric chloride from a mixture of phosphoric and hydrochloric acids provided the concentration of the latter is 6 molar. The ferric chloride free solution retains all phosphoric acid and a major portion of hydrochloric acid which can be separated by distillation. The separation can be as high as 95 per cent. The final product which is formed as a result of neutralization by ammonia contains 52.6 per cent P₂O₅, 27.25 per cent ammonia (Table 3).

Acknowledgement

Thanks are due to Dr. B. K. Banerjee, Additional Superintendent of this Division, for his keen interest in this investigation.

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The oxidation behaviour of ferrophosphorus has been studied with particular reference to the effect of manganese substitution in the ferrophosphorus lattice. It has been observed that oxidation of ferrophosphorus occurs in the range of 1000-1100°C. The major portion of phosphorus can be oxidized to P_2O_5 on heating upto 6 hr. in the oxidation temperature. In case of ferromanganophosphorus, this oxidation temperature is lowered down to 600-700°C. The kinetic parameters for their oxidation process have been found out experimentally. The oxidation is found to be exothermic in nature and follows the first order reaction kinetics. Their activation energy is in the range of 14.72-4.04 K. cal/mole. The activation energy of ferrophosphorus is higher than that of ferromanganophosphorus. This may indicate that the oxidation energy decreases with incorporation of manganese in the ferrophosphorus lattice. However, this low value may also be due to less quantity of phosphorus in it.

Roasting of Ferro- and Ferromangano-Phosphorus and their Oxidation Kinetics

By H. ROY AND S. K. ADHYA,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

It has been reported by Roy *et al*^{1,2} that almost all the phosphorus of phosphatic rocks or basic slags can be extracted in the form of ferro- or ferromangano-phosphorus with P_2O_5 content 56.5 and 12.5 per cent (24.66 and 5.4 per cent as phosphorus) respectively.

The main advantage of this concentration over the other processes is that constituents other than iron, manganese and phosphorus can be eliminated completely from the starting raw materials. But the success of this concentration procedure lies in evolving a suitable process of winning the phosphorus from the ferro- or ferromangano-phosphorus mass. So far no work in this direction has come to the notice of the present authors, who have made an attempt to prepare phosphoric acid from ferrophosphorus mass by a dissolution and solvent extraction process¹. Although extraction of phosphoric acid is possible by such a process yet it cannot perhaps be implemented on a commercial scale unless the by-product, viz. ferric chloride, which is produced in a large quantity, finds its market.

The other alternative, which seems economical, is the roasting of these ferrophosphorus masses similar to that of pyrites. Considering this, an attempt has been made here to study the roasting characteristics of ferro- and ferromangano-phosphorus with particular reference to their oxidation kinetics.

Experimental

Two samples taken for this investigation were (i) ferrophosphorus and (ii) ferromangano-phosphorus, prepared from iron-rich rock phosphates and basic slags respectively. The procedure for their preparation was developed in this laboratory^{1,2}. The chemical composition of these samples are given in the Table 1, P_2O_5 contents of the samples 1 and 2 being 51.1 and 7.2 per cent respectively.

Differential Thermal Analysis: DTA of both the samples was carried out in a fully automatic model of Linseis instrument in the temperature range 30-1200°C. The thermocouples were platinum, platinum-rhodium (13 per cent) and the sample holders were made of platinum cups. The rate of heating was controlled at about 10°C/min. by a programme controller. α -alumina was used as

TABLE 1—CHEMICAL COMPOSITION OF FERRO- AND FERROMANGANO-PHOSPHORUS MASS, %

Constituents	Sample 1	Sample 2
P_2O_5	51.1	7.2
Fe	76.0	78.6
Mn	Nil	19.2

a reference substance. The thermograms are shown in the Fig. 1. The peak temperatures are given in the Table 2.

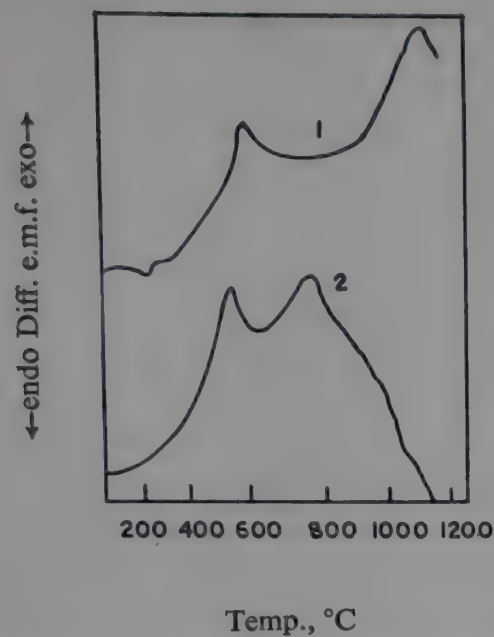


Fig. 1—DTA Thermograms of Ferrophosphorus Samples
1. Ferrophosphorus
2. Ferromangano-phosphorus

TABLE 2—DTA AND DTGA DATA OF FERRO- AND FERROMANGANO-PHOSPHORUS MASS

Sample	DTA Peak Temperatures & Their Nature, °C		DTGA De-composition Range, °C	Activation Energy Kcal/mole
	Endothermic	Exothermic		
1.	Nil	290 - w 620 - m 1150 - s	550 to 800 - m 850 onward - s	14.72
2.	Nil	550 - 850 - s	600 to 1000 - s	4.04

s - strong, m - medium, w - weak

Derivative Thermogravimetric Analysis (DTGA): Thermogravimetric analysis of these samples was carried out in an apparatus fabricated in this laboratory in the temperature range 30-1000°C. The plots of dw/dt against T are shown in the Fig. 2 and the decomposition ranges are given in the Table 2.

Kinetic Study: The oxidation of ferrophosphorus and ferromangano-phosphorus was studied at three different temperatures viz. 1000, 1100, 1200°C and 800, 900, 1000°C respectively. About 2g. of each sample was taken in a magnesite container (made from magnesite brick) and

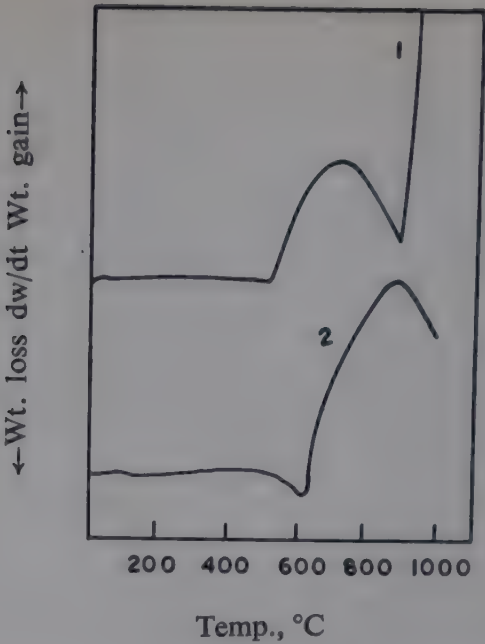


Fig. 2—DTGA Thermograms of Ferrophosphorus Samples
1. Ferrophosphorus
2. Ferromangano-phosphorus

heated at different specified temperatures in oxidizing atmosphere (air) for 1, 2, 3, 4, 6 and 12 hours. The P₂O₅ content of the heat-treated product was determined by following the procedure of Kumar *et al*³. The P₂O₅ content vs. time of heating at each temperature is shown in the Figs. 3A and 3B.

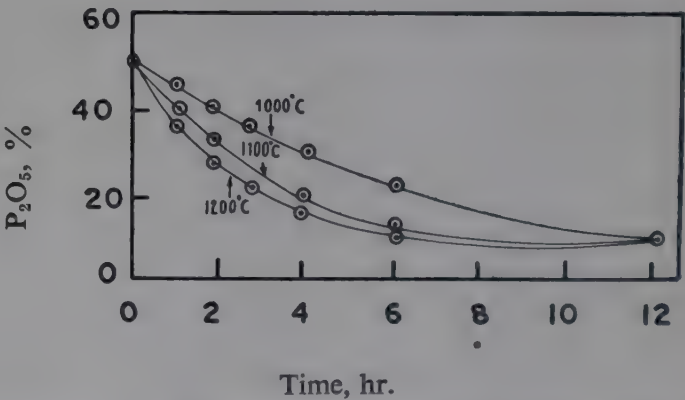


Fig. 3A—P₂O₅ Vs. Time of Heating of Ferromangano-phosphorus

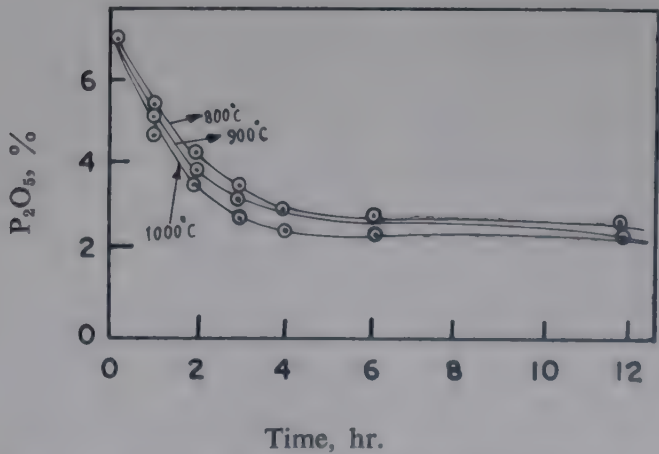


Fig. 3B—P₂O₅ Content Vs. Time of Heating of Ferrophosphorus

The order of reaction was ascertained by calculating rate constant (K) from these data with the help of standard equations derived for first, second and third order reactions respectively which are as follows⁴:

$$K = \frac{1}{t} \ln \frac{C_0}{C} \quad \dots \text{First order}$$

$$K = \frac{1}{t} \left(\frac{1}{C} - \frac{1}{C_0} \right) \quad \dots \text{Second order}$$

$$K = \frac{1}{2t} \left(\frac{1}{C^2} - \frac{1}{C_0^2} \right) \quad \dots \text{Third order}$$

where K = rate constant, t = time of heating, C₀ = initial concentration of P₂O₅ and C = final concentration of P₂O₅.

From the known values of t, C and C₀, K was calculated. The values of K are given in the Table 3. The activation energies for the oxidation of these samples were calculated graphically from the plot of log₁₀ K against $\frac{1}{T}$ of Arrhenius equation, which is represented by

$$\log_{10} K = - \left(\frac{0.4343E}{R} \right) \frac{1}{T} + \log_{10} A \quad (1)$$

where E = activation energy,

log₁₀ A = frequency factor.

The graphs are shown in Fig. 4 and energy values in Table 2.

Results and Discussion

It is evident from DTA thermograms (Fig. 1) that one exothermic peak at 1150°C starting from 850°C is

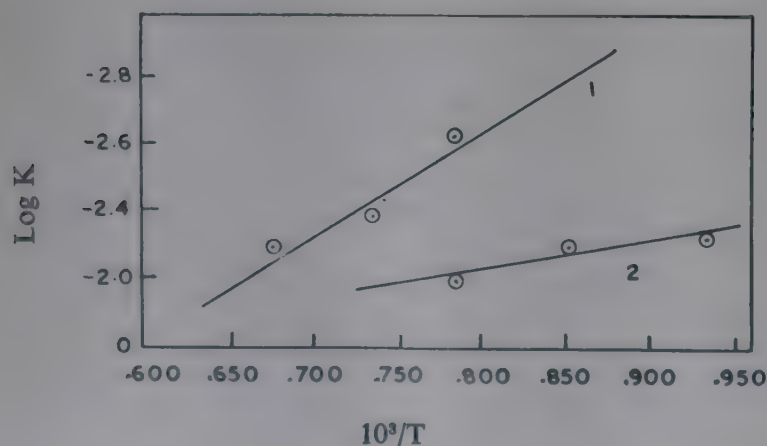
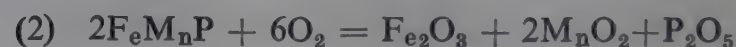
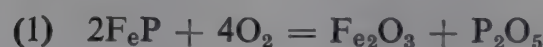


Fig. 4—Arrhenius Plot of Ferrophosphorus Samples
1. Ferrophosphorus
2. Ferromangano-phosphorus

present in the case of sample 1. This peak temperature is much less in sample 2 and the peak appears in the range 550-850°C. Sample 1 is known to be ferrophosphorus and sample 2 a ferromangano-phosphorus compound^{1,2}. This peak also is in agreement with their DTGA analysis. DTGA thermogram shows a sharp decomposition step starting at 850°C in the case of sample 1 and at 600°C in the case of sample 2 (Fig. 2). It may thus be inferred that the oxidation temperature is reduced if ferrophosphorus is alloyed with manganese.

It is interesting to mention here that two other exothermic peaks at 290 and 620°C appear in the DTA thermogram of sample 1. A medium size decomposition step in the range of 550-800°C, which corresponds to the later DTA peak of this sample, is also present in its DTGA thermogram (Fig. 2). These peaks are characteristics of magnetite. This shows that magnetite is present in small proportion in the ferrophosphorus sample. It is worthwhile mentioning here that there is practically no decomposition of phosphorus during oxidation of this magnetite (P₂O₅-50 per cent after heat treatment at 700°C for 6 hr. as against 51.1 per cent of the original sample).

From the kinetic parameters (Table 3), it is evident that oxidation of both ferro- and ferromangano-phosphorus follows the first order reaction. It has also been found that P₂O₅ is formed as a result of this oxidation. Their reaction may thus be represented by:



The gain in weight of both the samples due to oxidation as observed by their thermogravimetric analysis confirms the formation of metallic oxides.

It is interesting to mention here that a small proportion of phosphorus is still retained in both the cases even when they are heated for a considerable period at the oxidizing temperature. The P₂O₅ content of the samples 1 and 2 has been found to be constant after 6 and 4 hr. of heating respectively at all experimental temperatures (Figs. 3A and 3B). Possibly a little amount of iron or iron and manganese phosphate is formed as a result of oxidation. However, further work is in progress to ascertain the phases formed as a result of oxidation.

The activation energy for the oxidation of ferrophosphorus (sample 1) and ferromangano-phosphorus (sample 2) has been found to be 14.7 and 4.04 Kcal/mole, respectively. It indicates that presence of manganese in

TABLE 3—KINETIC DATA OF FERROPHOSPHORUS AND FERROMANGANO-PHOSPHORUS MASSES

Reaction Order	Time, hr.	Rate Constant, min ⁻¹					
		Sample 1			Sample 2		
		1000°C	1100°C	1200°C	800°C	900°C	1000°C
First	1	—	—	—	4.6×10^{-3}	5.1×10^{-3}	6.07×10^{-3}
	2	—	—	—	4.5×10^{-3}	5.1×10^{-3}	6.01×10^{-3}
	3	2.25×10^{-3}	3.95×10^{-3}	4.67×10^{-3}	4.2×10^{-3}	4.6×10^{-3}	5.6×10^{-3}
	4	2.28×10^{-3}	3.93×10^{-3}	4.77×10^{-3}	—	—	—
	6	2.28×10^{-3}	4.06×10^{-3}	4.61×10^{-3}	—	—	—
Second	1	—	—	—	7.15×10^{-4}	8.29×10^{-4}	10.16×10^{-4}
	2	—	—	—	8.26×10^{-4}	9.7×10^{-4}	12.22×10^{-4}
	3	5.44×10^{-5}	1.13×10^{-4}	1.43×10^{-4}	8.66×10^{-4}	10.25×10^{-4}	13.72×10^{-4}
	4	5.91×10^{-5}	1.2×10^{-4}	1.7×10^{-4}	—	—	—
	6	6.88×10^{-5}	1.8×10^{-4}	2.2×10^{-4}	—	—	—
Third	1	—	—	—	1.15×10^{-4}	1.35×10^{-4}	1.72×10^{-4}
	2	—	—	—	1.56×10^{-4}	1.93×10^{-4}	2.59×10^{-4}
	3	2.3×10^{-6}	3.5×10^{-6}	4.6×10^{-6}	1.85×10^{-4}	2.35×10^{-4}	3.57×10^{-4}
	4	1.59×10^{-6}	4.5×10^{-6}	7.1×10^{-6}	—	—	—
	6	2.2×10^{-6}	9.4×10^{-6}	13.1×10^{-6}	—	—	—

ferrophosphorus lattice decreases the oxidation energy considerably. This low value may be due to the presence of less quantity of phosphorus in the sample.

Acknowledgement

Thanks are due to Dr. B. K. Banerjee, Additional Superintendent of this Division, for his keen interest in this investigation.

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The activity of zinc oxide with respect to absorption of hydrogen sulphide gas has no direct dependence either on the surface area or pore volume of the absorbent. It has been found that the activity of the oxide is greatly influenced by the specific pore size distribution. Oxides having maximum aggregation of pores between 300 and 500Å appear to be most active.

Dependence of Desulphurization Activity of Zinc Oxide on its Structural Parameters

By P. K. GAUR, A. R. CHATTERJEE, M. S. CHHABRA
AND N. B. BHATTACHARYYA,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

The recent advances in petroleum technology and the increasing availability of cheap light distillates has led to the development of naphtha-based fertilizer industries. These feedstocks, depending on their boiling range, contain different sulphur compounds, viz. mercaptans, organic sulphides R-S-R, disulphides R-S-S-R, carbon disulphide, thiophene and its homologues. The sulphur content of the feed increases with increase in the boiling range¹. Since the catalyst normally employed for the gassification for these feedstocks are sensitive to sulphur, it has necessiated a prior treatment of the feed for the sulphur removal. The desulphurization of liquid hydrocarbon is achieved in two steps, viz. (1) the hydrogenation of organic sulphur compounds to the corresponding hydrocarbon and hydrogen sulphide and (2) absorption of hydrogen sulphide formed during hydrogenation by some suitable absorbates.

It is known that hydrogen sulphide is absorbed quantitatively by hot beds of Luxmasse, manganese and zinc oxides^{2,3}. For removal of hydrogen sulphide from naphtha vapours, a contact mass containing 90-95 per cent zinc oxide is generally used. To suit the industrial requirement, the material is used in an extruded, tablet or globule form. Zinc oxide is actually a solid reactant which reacts with hydrogen sulphide producing zinc sulphide and water vapour and as such it may appear that the activity of zinc oxide should be proportional to its ZnO content. But the commercial varieties, although having similar zinc oxide contents, differ widely in activity and capacity. It appears that the relative activity

depends on structural parameters which make the oxide surface accessible to hydrogen sulphide.

In this investigation, a comparative study has been made for the evaluation of activity and life of four samples of catalyst in a flow system. Out of these, one has been prepared in this laboratory while the others are commercial catalysts. The surface area, pore volume and pore size distribution have been determined and attempts have been made to draw a relation between the activity and the above structural parameters.

Experimental

In this investigation four samples of catalyst were studied. The sample 1 was prepared in this laboratory by mixing zinc oxide with iron in the form of a nitrate. The mixed mass was heat-treated between 250 and 300°C, ground, and from the powdered mass globules of 3-5 mm. diam. were prepared. The other three samples were imported.

The activity tests were carried out in a bench-scale glass reactor, which was electrically heated with suitable controls for maintaining the desired temperature. Approximately 25 to 30g. of catalyst depending on bulk density was charged in the reactor. Temperature was recorded by a thermocouple inserted in the exit side of the catalyst bed. Nitrogen was used as a carrier gas. Hydrogen sulphide of known purity was dosed in the carrier gas to get the desired sulphur concentration. The gas leaving the reactor was passed through a glass wool filter and later it was scrubbed through an acidic

cadmium salt solution for estimation of the unabsorbed hydrogen sulphide.

Surface area was determined by following the usual BET method and pore volume by helium densitometer. Pore size distribution was determined by Aminco-Winslow mercury porosimeter (model No. 5-7170), which is a hydraulic instrument wherein pressures from 0 to 5000 psi can be applied on mercury and pore size down to 350Å can be measured. The pore diameter is related to pressure as below:

$$D = \frac{175}{P},$$

where D is pore diameter in microns and P equals absolute pressures (lb./sq. in.).

The effect of space velocity on hydrogen sulphide removal was examined by varying it from 1000 to 8000. For determining the initial breakthrough space velocity, the hydrogen sulphide concentration was kept constant at 500 ppm vol./vol. and space velocity was increased gradually till traces of hydrogen sulphide appeared in the exit gas. This very space velocity was treated as the breakthrough space velocity for that particular concentration of hydrogen sulphide and reaction temperature. After determining the breakthrough, space velocity was further increased in steps of 500 to determine the rate of hydrogen sulphide absorption beyond this space velocity. Later on, the zinc oxide mass was reacted with hydrogen sulphide to sulphide in steps of 10 per cent by weight on dry basis by dosing hydrogen sulphide at a higher rate. After reaching the desired percentage of sulphide content, the breakthrough space velocity was determined again as mentioned above.

Results and Discussion

From the results in Table 1 and Fig. 1, it may be observed that sample 1 is the most active out of the four catalysts studied. At space velocity of 8000 the hydrogen sulphide concentration in the treated gas was nil for sample 1 and traces for samples 2 and 3. However, sample 4 exhibited comparatively poor activity. The slip of hydrogen sulphide through the catalyst bed occurred at 3000 space velocity and at 4000 space velocity the hydrogen sulphide concentration in the exit gas was 13 ppm vol./vol. The hydrogen sulphide content in the purified gas increased gradually with space velocity beyond the breakthrough in all the four cases investigated. In general, the breakthrough space velocity decreased with increase in the sulphur content of the oxide mass. At higher sulphur content of the used

mass, difference in activity of various samples was magnified (Table 1).

The affinity of zinc^{4,5} for sulphur is known. According to Schürman⁵, this affinity is greater than that of nickel, cobalt, iron, arsenic, thorium and manganese. Zinc in the form of oxide reacts with hydrogen sulphide forming zinc sulphide and water. At high temperature, it removes hydrogen sulphide quantitatively from fuel, synthesis and other gases⁶.

The absorption of hydrogen sulphide by zinc oxide is purely a chemical reaction. According to the law of mass action, the rate of reaction should depend on partial pressure of hydrogen sulphide only, zinc oxide being in the solid phase. Although the zinc oxide content of the commercial catalysts (samples 2 to 4) are almost identical their activity and capacity differ widely under the same process conditions. It is very likely that the activity of the zinc oxide is dependent on its specific surface area and other reaction parameters. So the rate of reaction should be proportional to the partial pressure of hydrogen sulphide, surface area of catalyst and time of contact. Since the partial pressure of hydrogen sulphide and time of contact has been kept constant for a particular set of experiments, the hydrogen sulphide removal rate should be directly proportional to the surface area.

It may be seen from results (Tables 1 and 2) that the specific surface area of zinc oxide has no relation either with the rate of removal or total absorption capacity of

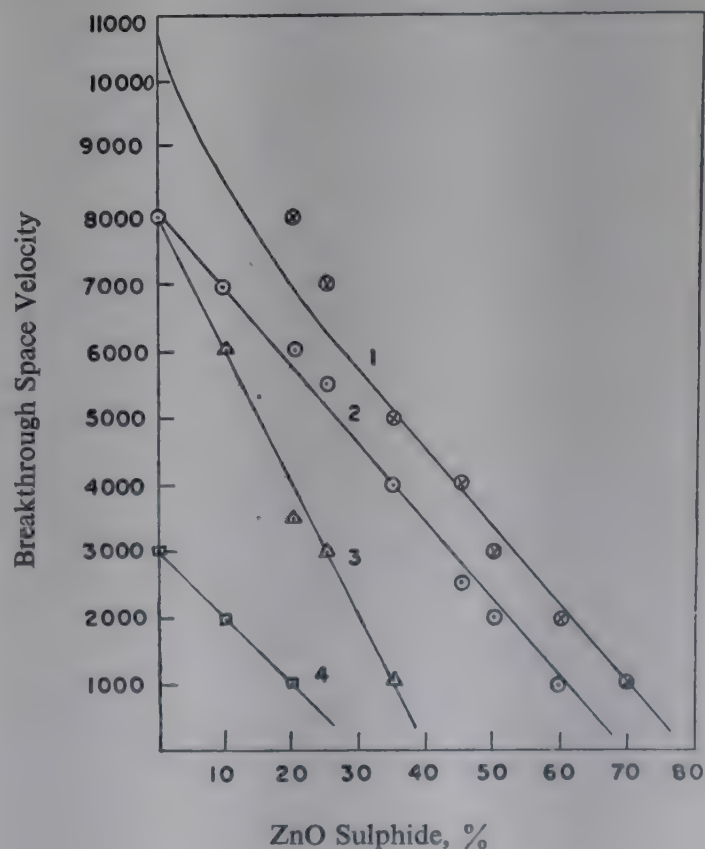


Fig. 1

the oxide. Specific surface areas of samples 1, 2, 3 and 4 are 9, 31.05, 24.65 and 4.03 m²/g. respectively. Although the surface area of sample 1 (prepared in this laboratory) is only 9 m²/g, yet it gave the best performance out of the four samples investigated. The initial activity of samples 2 and 3 was same but with increase in the sulphide content of the catalyst mass their capacity as well as rate of hydrogen sulphide absorption differed appreciably. (Fig. 1, Table 1). When 20 per cent of the oxide was reacted to sulphide, breakthrough space velocities for samples 1, 2, 3 and 4 were 8000, 6000, 3500 and 1000 respectively; at 35 per cent sulphide con-

tent of samples 1, 2 and 3 they were 5000, 4000 and 1000 respectively. On increasing the sulphide content to 60 per cent by weight for samples 1 and 2, the breakthrough occurred at 2000 and 1000 respectively. Even when 70 per cent of the oxide was converted to sulphide sample 1 can be operated at 1000 space velocity for quantitative desulphurization of the feed gas.

From above results, it appears that the total surface area of zinc oxide, which is constituted by the pore walls, is not easily accessible to reacting gas molecules. The availability of surface appears to be limited by certain lower and upper limits of pore diameters. From Table 2,

TABLE 1—REMOVAL OF HYDROGEN SULPHIDE BY ZINC OXIDE FROM NITROGEN

Temperature of the Reactor = 400°C
H₂S in the Inlet Gas = 500 ppm
Carrier gas used was nitrogen

Zno Sulphide, %	Sample 1		Sample 2		Sample 3		Sample 4	
	Space Velocity	H ₂ S in Exit	Space Velocity	H ₂ S in Exit	Space Velocity	H ₂ S in Exit	Space Velocity	H ₂ S in Exit
Fresh	8000	Nil	8000	Traces	8000	Traces	3000	Traces
							3500	4 ppm
							4000	13 ppm
10	6000	Nil	7000	Traces	6000	Traces	2000	Traces
							2500	6 ppm
							3000	18 ppm
20	6000	Nil	6000	Traces	3500	Traces	1000	Traces
							1500	5 ppm
							2000	14 ppm
25	7000	Traces	5500	Traces	3000	Traces	—	—
							—	—
							—	—
35	5000	Traces	4000	Traces	1000	Traces	—	—
							—	—
							—	—
45	4000	Traces	2500	Traces	—	—	—	—
							—	—
							—	—
50	3000	Traces	2000	Traces	—	—	—	—
							—	—
							—	—
60	2000	Traces	1000	Traces	—	—	—	—
							—	—
							—	—
70	1000	Traces	—	—	—	—	—	—
							—	—
							—	—

TABLE 2—PHYSICAL PROPERTIES OF DIFFERENT ZINC OXIDE CATALYST SAMPLES

Sample Number	Bulk Density g./cc	Surface Area, m ² /g.	Pore Volume, cc/g.	Pore Size Distribution, %				
				4-175 Å	175-300 Å	300-400 Å	400-500 Å	500-75000 Å
1	1.25	9.0	0.3196	14.3	6.2	10.7	27.1	41.7
2	1.15	31.05	0.3339	12.35	36.51	9.61	10.0	31.53
3	1.55	24.65	0.2093	90.46	3.68	1.41	2.41	2.04
4	1.45	4.03	0.2037	4.61	0.0	0.0	1.32	94.07

it may be seen that sample 1 has 37.8 per cent pores between 300-500Å corresponding figures for sample 2, 3 and 4 are 19.61, 3.81 and 1.32 per cent respectively. A linear relationship between the activity and this pore size range seems to exist, at least qualitatively. It appears from studies of the structural properties of the catalyst (Table 2) that most suitable pore radius for the reaction lies in the range of 300-500Å. Pores in the range of 500-75000 are probably not so much effective and are responsible for the poor performance of sample 4, which contains 94 per cent of its total pores in that range. On the other hand, the pores in the lower range of 175-300Å are also found to be effective but to a lesser extent compared to those in the range 300-500Å.

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The hydrogen sulphide absorption rate and capacity of desulphurization mass were found to depend on the active iron content only and independent of other constituents. The rate of hydrogen sulphide absorption and the capacity of the synthetic and diluted oxides remain practically unchanged even when the accumulated sulphur reaches 70 and 50 per cent respectively. For synthetic oxide, outside revivification is essential to regain full activity and capacity, whereas in case of diluted mass outside revivification appears to have little advantage over that *in situ*. The rate of hydrogen sulphide absorption does not improve by increasing the moisture content of the oxide above 5 per cent.

A Study of Desulphurization Oxide

By M. SUNDARAM AND N. B. BHATTACHARYYA,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Purification of industrial gases from sulphur compounds is an important step in gas-making industry. The limits of the sulphur compounds in purified gas is strongly adhered to due to their corrosive and poisonous nature. Hydrogen sulphide is the principal sulphur compound and it constitutes the bulk of impurities in gases manufactured from coal or fuel oils.

The hydrated oxides of iron have been used since long for the removal of hydrogen sulphide from industrial gases. The process, although involving considerable material handling, is still today one of the cheapest and popular method in gas-processing industry. The principles involved are the reaction of hydrogen sulphide with iron oxide in presence of moisture, the reaction media is maintained on the alkaline side and pH should be preferably between 8-10. The second step is the regeneration of sulphide in presence of oxygen to free iron oxide and sulphur. The principal reactions involved are



The above reactions may take place simultaneously in the box keeping the iron oxide in the active state where a small amount of oxygen is injected and the liberated sulphur goes on accumulating in the mass. This process, however, cannot continue indefinitely, because with increasing sulphur content in the mass there is a tendency of cake formation resulting in increased pressure drop across the system and consequent deterioration of the efficiency of the box. The caking of the mass can be prevented and its absorption rate and capacity main-

tained by periodic discharge of the spent mass for revivification. Frequent discharge of the spent mass for revivification, however, involves considerable material handling, thus adding up the cost. It is reported that it has been possible to run the purification system efficiently even with sulphur content as high as 50 per cent¹ in the spent mass. But in actual practice this limit is seldom achieved.

In dry-box purification, Luxmasse, Bogore and synthetic oxide are commercially used. Luxmasse and Bogore are imported materials. Dust catcher² dust and iron ore have been reported as effective substitute of Luxmasse but their commercial success are yet to be proved. Synthetic oxides, developed and manufactured indigenously, have successfully replaced imported oxides. An investigation for a substitute of synthetic oxides, which may be cheaper and easily available, is already in progress.

There are references in literature on the dry-box purification method practiced in commercial units. But systematic data on comparative study on activity related to composition, increasing sulphur accumulation in purifying mass, are not available. In view of the above, studies have been undertaken to ascertain the following aspects. (1) Dependence of activity on composition; (2) Effect of increasing sulphur content in the purifying mass on activity and capacity; (3) comparative efficiency of regeneration—outside reactor and *in situ*; and (4) effect of moisture content on activity and capacity.

Experimental

Materials: The following samples were taken for study: (1) synthetic iron oxide, (2) diluted mass³, (3) Luxmasse and (4) Dorr thickener sludge, which is a waste product from blast furnace.

Activity Test: For determination of hydrogen sulphide absorption capacity, approximately 2g. of dry mass was taken and mixed with requisite amount of saw dust to make the mixed mass fluffy. A few drops of water were added to make the mass just moist. This mixed mass is now filled in a previously weighed Nesbitt tube. Fused calcium chloride is packed at the top of the tube so that moisture may not escape from the system. Hydrogen sulphide is now passed through the tube at controlled rate and weight of the tube is noted at fixed intervals.

Results and Discussion

Activity and Composition: The results on the rate of hydrogen sulphide absorption by different samples and their capacity are shown in Fig. 1. The compositions of the samples are given in Table 1.

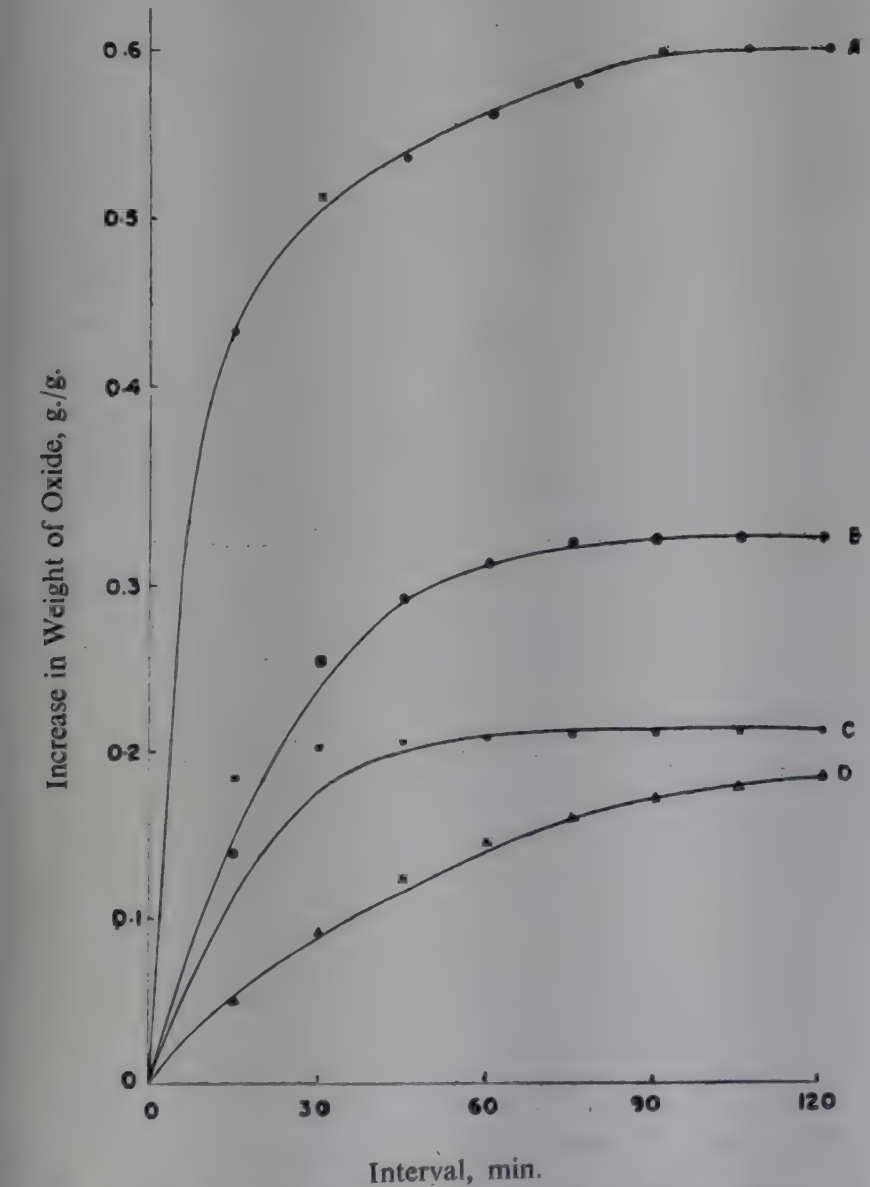


Fig. 1—Comparison of Relative Activities of Sindri Oxide (A), Luxmasse (B), Diluted Oxide (C) and Dorr Thickener Sludge (D)

TABLE 1—COMPOSITIONS, % (W/W)

Sample No.	1	2	3	4
Loss in Ignition, (900°C)	6.00	13.07	17.20	21.60
Silica and Insolubles	—	5.02	6.10	9.81
Mixed oxide (R ₂ O ₃)	—	35.16	66.52	60.82
Iron oxide (Fe ₂ O ₃)	94.01	34.20	53.60	52.85
Lime (CaO)	—	23.66	4.73	4.98
Sulphate (SO ₃)	Traces	24.12	—	—
Carbon dioxide (CO ₂)	—	1.25	—	—

It may be seen from the composition that precipitated oxide (sample 1) contains only hydrated ferric oxide, while the remaining samples contain silica, lime, sulphur and volatile matter in various proportions. Luxmasse and Dorr thickener sludge are almost identical with respect to their composition.

In the cases of synthetic oxide, diluted mass and Luxmasse, hydrogen sulphide absorption is proportional to their ferric oxide content. However, other constituents do not appear to have any influence on either the capacity or rate of absorption of hydrogen sulphide. The whole of the iron oxide content of these three samples are active for hydrogen sulphide absorption. But the activity of Dorr Thickener sludge is rather poor though its ferric oxide content is as high as 52.85 per cent, of which only 45.9 per cent are available for reaction with hydrogen sulphide. Not only the capacity of Dorr Thickener sludge is low, but the rate of hydrogen sulphide absorption is also comparatively slow. This poor activity of Dorr Thickener sludge may be due to the fact that this mass, which is a waste product of blast furnace has been exposed to very high temperature which might have converted most of the oxide inactive for absorption of hydrogen sulphide.

It is also found that the rate of hydrogen sulphide absorption varies with active ferric oxide content of the individual sample. The higher the active iron content, faster is the rate of absorption (Fig. 1).

Effect of Increasing Sulphur Content on Activity and the Advantage of Revivification Inside and Outside the Reactor: For evaluating the effect of increasing sulphur content on the activity and the advantage of revivification inside and outside the reactor, two samples, viz. synthetic oxide and diluted mass, containing 94.01 and

34.20 per cent ferric oxide respectively were studied. The results are given in Figs. 2-5.

The rate of hydrogen sulphide absorption by oxide remains practically unaffected with increasing sulphur content in the used mass when the revivification is done

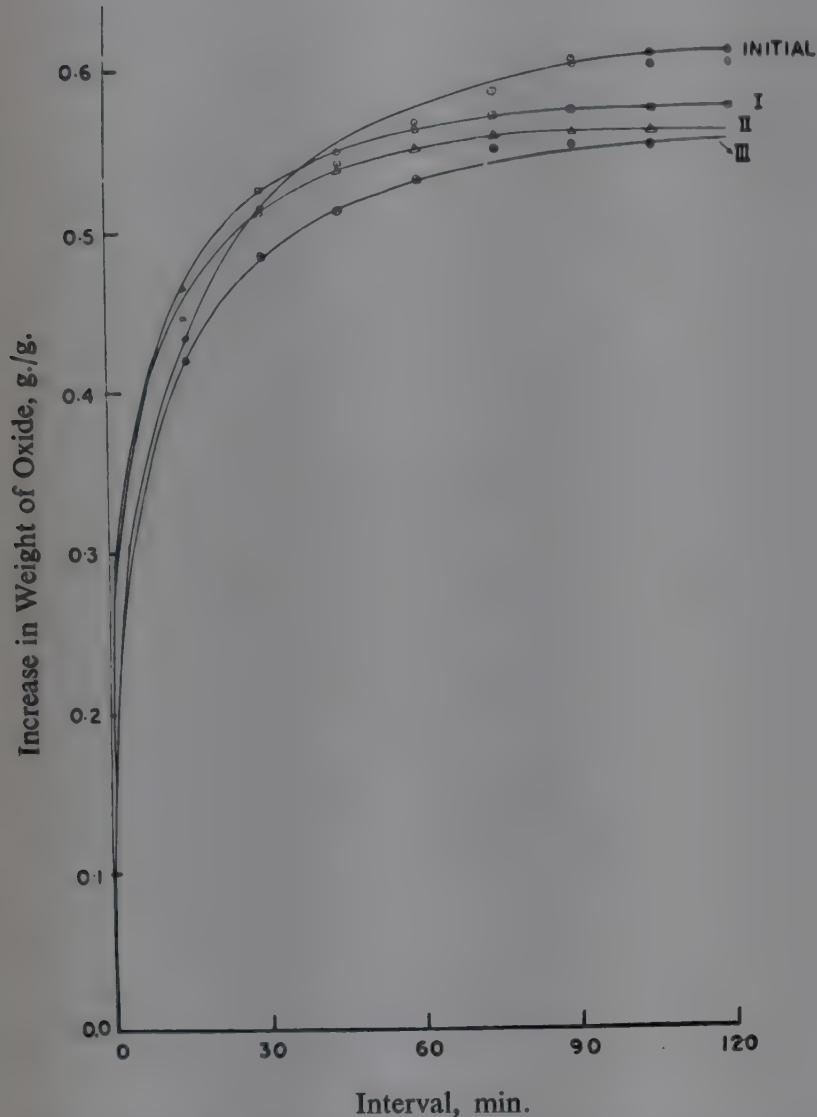


Fig. 2—Rate of Hydrogen Sulphide Absorption after Repeated Foulings
[Revivification done outside Reactor Tube]

outside the reactor. The freshly charged synthetic oxide when exposed to hydrogen sulphide, absorption is 60 per cent. In second, third and fourth stages of sulphidation, sulphur absorption is 57, 56, and 55 per cent res-

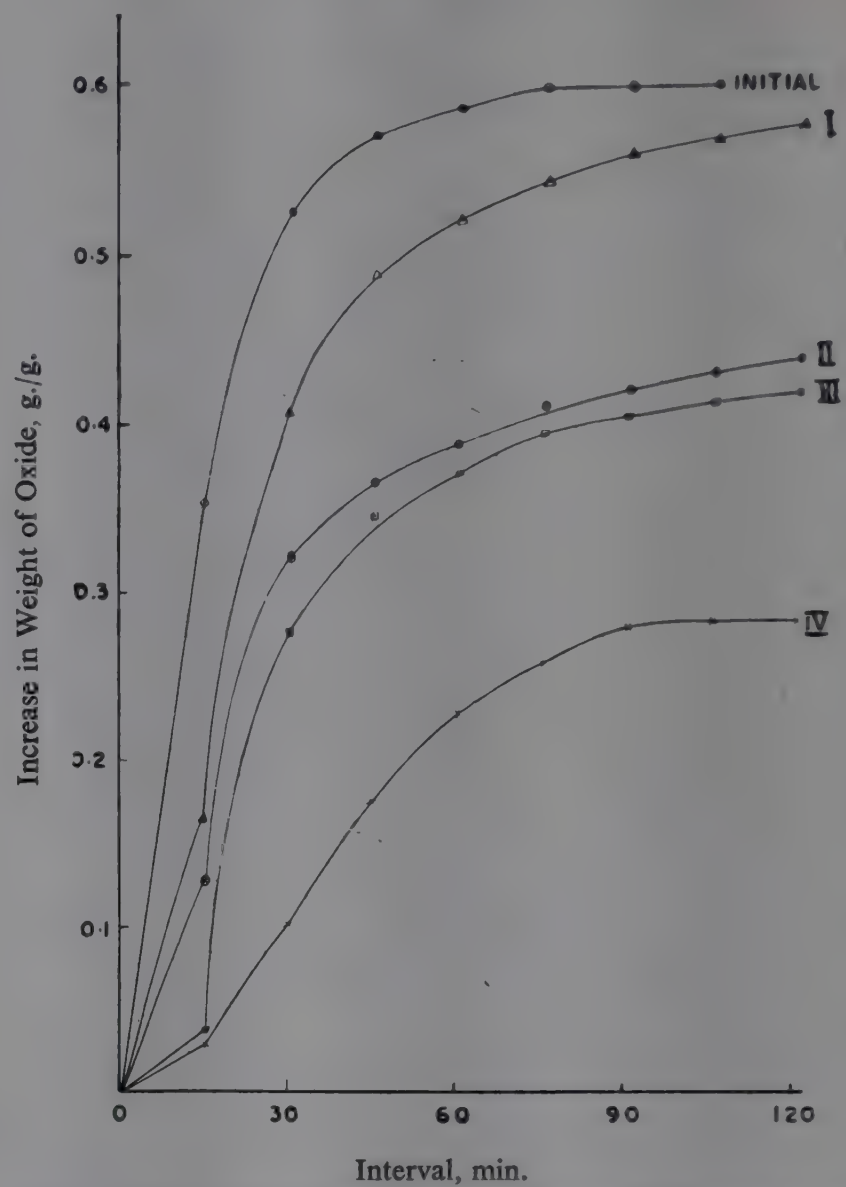
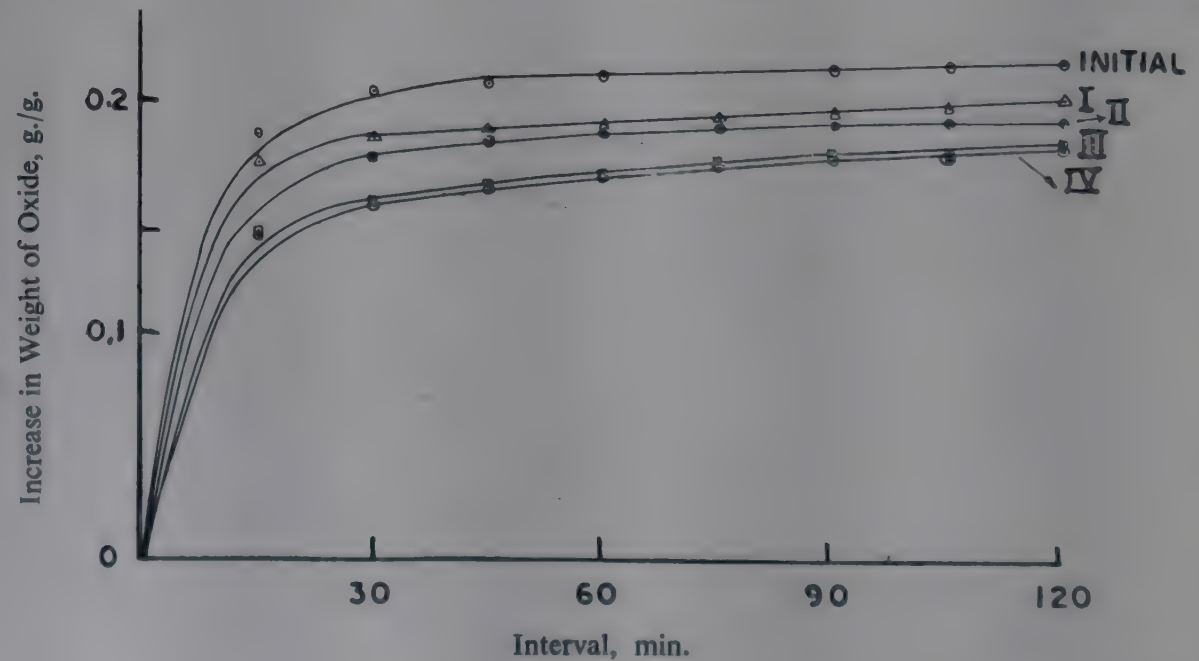


Fig. 3—Sindri Oxide: Rate of Hydrogen Sulphide Absorption after Repeated Foulings
---- [Revivification done inside Reactor Tube]

Fig. 4—Diluted Mass: Rate of Hydrogen Sulphide Absorption after Repeated Foulings
[Revivification done outside Reactor Tube]



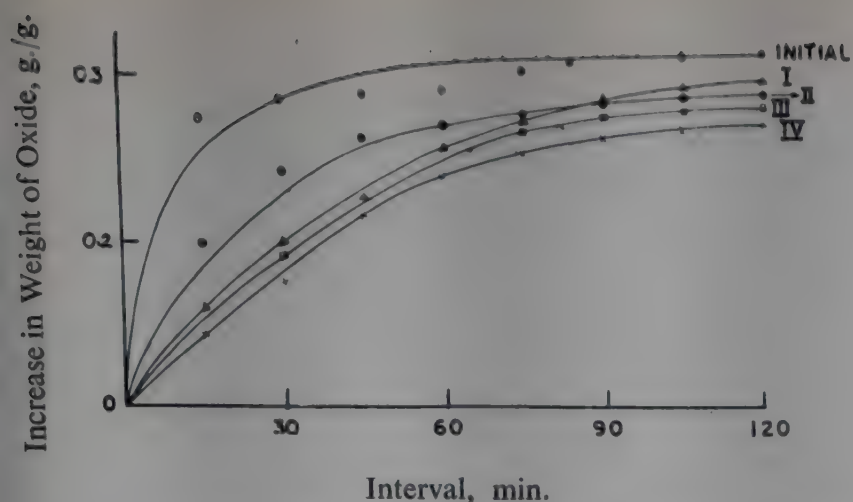


Fig. 5—Diluted Mass: Rate of Hydrogen Sulphide Absorption after Repeated Foulings

[Revivification done inside Reactor Tube]

pectively. Sulphur content of the fouled mass after the fourth exposure is nearly 70 per cent; the corresponding figure for diluted mass (Fig.4) after the fifth stage of fouling is 50 per cent though iron content of the fresh oxide is almost one third (Table 1) to that of synthetic oxide.

The results were interesting when the regeneration of the oxides are done inside the reactor (Figs. 3 and 5). In case of synthetic oxide, when the regeneration was done inside the reactor, the rate of hydrogen sulphide absorption and its capacity dropped appreciably in each cycle of operation (Fig. 3). In contrast, though the rate of hydrogen sulphide absorption by dilute mass dropped (Fig. 5), its capacity remained practically unaffected whether the reacted mass is revivified inside or outside the reactor. The difference in the absorption rate and

capacity of the two oxides may be due to the difference in their physical characteristics. Though the free sulphur formed after oxidation may migrate ^{4,5} to the core of the oxide grain keeping it free for reaction, with increasing sulphur in the purifying mass, however, there may be masking effect and the access to active centres becomes more and more difficult. This restriction of approach to active surface is likely to slow down the reaction rate making the process of absorption sluggish. The effect of increasing sulphur content in the case of diluted mass is less prominent, which may be due to the fact that the active ferric oxide particles are more evenly spread on the diluent and there is enough room for accommodating the liberated sulphur keeping the oxide free and easily accessible to the reacting gases.

The above observation on the regeneration of the fouled mass shows that in the case of purifying mass rich in active ferric oxide content, it is essential to discharge it from the purifier box for complete oxidation of the sulphide for developing its full activity. However, in the case of a mass dilute with respect to ferric oxide content revivification inside the box appears to be adequate.

Effect of Moisture on Rate of Hydrogen Sulphide Absorption: For this study only one sample, viz. diluted oxide, was taken. The rate of hydrogen sulphide absorption was determined with dry oxide, and also with oxide containing 5, 10, 20 and 30 per cent moisture in the mass. The results are presented in Table 2. It may be seen that when the oxide is dry, reaction is slow but practically the whole of the ferric oxide content could be

TABLE 2—EFFECT OF MOISTURE ON THE RATE OF ABSORPTION OF HYDROGEN SULPHIDE

Time, min.	Increase in Weight of Oxide, g.				
	Moisture 0%	Moisture 5%	Moisture 15%	Moisture 20%	Moisture 30%
15	0.1429	0.1818	0.1794	0.1830	0.1798
30	0.1660	0.1936	0.1931	0.1942	0.1944
45	0.1838	0.1993	0.1982	0.1990	0.1980
60	0.1920	0.2020	0.2025	0.2018	0.2033
75	0.1994	0.2074	0.2051	0.2037	0.2080
90	0.2039	0.2090	0.2081	0.2064	0.2117
105	0.2051	0.2100	0.2108	0.2104	0.2126
120	0.2097	0.2106	0.2124	0.2123	0.2128

sulphided in 120 mins. only. With 5 per cent added moisture, the rate of absorption is very fast and 90 per cent of the oxide is fouled within 15 min. and thereafter the rate fell, which may be due to the accumulation of sulphided oxide on the surface making it difficult for the residual unreacted mass to come in contact with reacting gas. Moisture content more than 5 per cent appears to have no significant effect either on the rate of absorption or capacity of the oxide.

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An attempt has been made to determine surface areas of a number of silica gel supports, prepared by different methods on the basis of hydroxyl coverage of the surface. It is found that a direct relation exists between BET surface area and hydroxyl coverage of the surface owing to chemisorbed water molecules. These results are also corroborated by plotting the DTA peak and BET areas.

Nitrogen adsorption-desorption isotherms, average pore and particle sizes have also been studied and it has been found that they do not have any bearing on the hydroxyl coverage of unit gel surface.

Dependence of Hydroxylation on the Surface of Silica Gel Carriers

By R. N. TIWARI, S. R. NAIDU, N. C. GANGULI
AND S. P. SEN,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Silica is an important constituent in almost all types of petrochemical cracking catalysts. The composition and structure may vary from catalyst to catalyst. The method of preparation of catalyst support and the resultant nature of its surface are of vital importance because its properties in turn, play a major role in controlling the principal surface characteristics of the catalyst. It is, therefore, necessary to correctly evaluate the basic surface parameters and structural properties of silica gels.

Recent evidence from infrared spectroscopy of absorbed water molecules, summarized by Little¹, has clearly established the existence of hydroxyl group on

the silica gel surfaces. DeBoer and Vleekens² have shown that the residual water content of silica dried at 120°C is actually the chemisorbed water in the form of surface hydroxyl groups. They have also shown that this water can be determined by igniting silica at high temperatures. If this is so, it should be possible to determine the surface area of silica from a knowledge of the total number of hydroxyl groups by using a proper cross-sectional area value of a chemisorbed water molecule or corresponding hydroxyl groups. In the present work, it is proposed to calculate the surface areas from the total number of hydroxyl groups and from the area available to each hydroxyl group, compare these areas with BET and DTA

peak areas. Nitrogen adsorption-desorption isotherms, average pore and particle diameters have also been determined to investigate their influence on the hydroxylation of silica surfaces.

Experimental

Ten samples of silica gel were prepared with varying pore-volumes and residual water content. Samples A to E were prepared by running down sodium silicate solution to hydrochloric acid and varying the final pH of the solution from 0.6 to 1.8. The gelation was done at room temperature. After setting, the gels were washed free of chloride ions and then dried in the oven at 120°C, samples F to I were prepared similar to the sample D, but gelation was done at different temperatures. Sample J was prepared by adding 11 per cent sodium silicate solution to a 13°C per cent copper sulphate solution at room temperature. Setting was almost instantaneous, after which the gel was washed free of sulphate ions and finally dried at 120°C in the oven.

The residual water content, specific volume, apparent volume, pore volume, BET surface areas, average pore and grain diameters were determined. Residual water was determined by heating the dried samples to 1100°C. Pore volumes were calculated as the difference between the apparent and specific volumes. DeBoer and Vleeskens² equation, $V_s = 0.43 + 0.01 W$ was used to find out the specific volume where W is the percentage loss on ignition at 1200°C.

DeBoer and Vleeskens² have demonstrated that the residual water content of silica dried at 120°C is actually the chemisorbed water in the form of surface-hydroxyl groups. Hence, the following relation has been used to calculate the number of hydroxyl groups per 100 Å²

$N(OH)$, from the values of W and the specific surface area, S :

$$N(OH) = \frac{W \times 10^{-2} \times N}{S \times 10^{18} \times M/2} = \frac{2 \times 10^3}{3} \times \frac{W}{S},$$

where N is Avogadro number, M the molecular wt. of water and S is the specific surface area in m²/g. This also follows that the total number of hydroxyl groups $N_t(OH)$ /g. will be given by

$$N_t(OH) = \frac{2 \times 10^{23} \times w}{3},$$

where w is the wt. of residual water/g.

$N_t(OH)$ values were used to calculate the total area occupied by surface hydroxyl groups. The average pore diameter $\bar{R}$ and average particle diameter $\bar{D}$ were calculated from the following two relations:

$$\bar{R} = \frac{4 V_p}{S}; \quad \bar{D} = \frac{6 V_a}{S}$$

BET surface areas were calculated from the low temperature nitrogen adsorption-desorption isotherms with the help of an automatic instrument*. DTA runs on some of the samples were made in order to examine if any linear relationship could be obtained between the peak area and the hydroxyl coverage area.

Since two hydroxyl groups or one water molecule occupy 10.6 Å² the surface, the hydroxyl surface area can be obtained by using the following relation.

$$S(OH) = \frac{6.02 \times 10^{23} \times w \times 10.6}{18 \times 10^{20}} \text{ m}^2/\text{g} = \frac{3.53 \times 10^3}{w} \text{ m}^2/\text{g}.$$

Results

The results (Table 1) show the residual water content,

* Adsorptomat, manufactured by American Instrument Co.

TABLE 1

Silica Gel Sample	L.O.I. Wt. %	Specific Volume (V_s), cc/g.	Apparent Volume (V_a), cc/g.	Pore Volume (V_p), cc/g.	pH of Preparation	Setting Time, hr.
A	5.84	0.488	0.995	0.507	0.60	40
B	5.96	0.489	0.876	0.387	1.15	11
C	6.19	0.492	0.825	0.333	1.30	9.5
D	6.47	0.495	0.884	0.389	1.60	8.0
E	6.85	0.498	0.882	0.384	1.80	7.0
F(40°C)	5.95	0.489	0.896	0.407	1.60	2.0
G(60°C)	6.43	0.494	0.888	0.394	1.60	1.25
H(80°C)	6.07	0.491	0.892	0.401	1.60	0.50
I(97°C)	5.12	0.481	0.843	0.362	1.60	0.25
J	10.17	0.532	2.868	2.336	7.00	0.00

L.O.I.—loss on ignition.

TABLE 2

Silica Gel Sample	BET Area (S), m ² /g	Average Pore Diam. (D), Å	Average Grain Diam. (D), Å	DTA Peak Area, cm. ² /g.	No. of OH Groups/100Å, N(OH)	Total No. of OH Groups/g. N _t (OH) × 10 ²¹	Surface Covered by OH Groups Using Mean 12.5Å ² as Area Available to Each OH Group, m ² /g.	Surface Covered by OH Groups Using 10.6 Å ² for 2, OH Groups, m ² /g.
A	480	42.25	124.37	6.77	8.11	3.89	486.25	206.15
B	495	31.27	106.18	7.03	8.02	3.97	496.25	210.38
C	510	26.11	97.05	7.19	8.09	4.12	515.00	218.50
D	530	29.35	100.07	7.63	8.13	4.31	538.75	228.39
E	565	27.18	93.66	8.25	8.08	4.56	570.00	241.80
F(40°C)	499	32.62	107.73	6.73	7.94	3.96	495.00	210.03
G(60°C)	525	30.01	101.48	7.69	8.16	4.28	535.00	226.97
H(80°C)	526	30.49	101.74	8.05	7.69	4.04	505.00	214.27
I(97°C)	542	26.71	93.32	8.42	6.29	3.41	426.25	180.73

specific and apparent volumes, pore volumes, pH of preparation and gelation time. Table 2 includes the values of BET surface area, average pore and particle diameters, DTA peak areas, total number of surface hydroxyl groups and surface areas of the gels on the

basis of hydroxyl group coverage area and water molecule orientation areas. The surface area results shown in the last but one column (Table 2) have been calculated on the basis of a mean area value available (12.5Å²) for each OH group on the surface.

Plots of some typical adsorption-desorption isotherms and DTA thermograms are shown in Figs. 1 and 2 respectively.

The plots of percentage residual water content and BET areas against DTA peak areas are shown in Fig. 3.

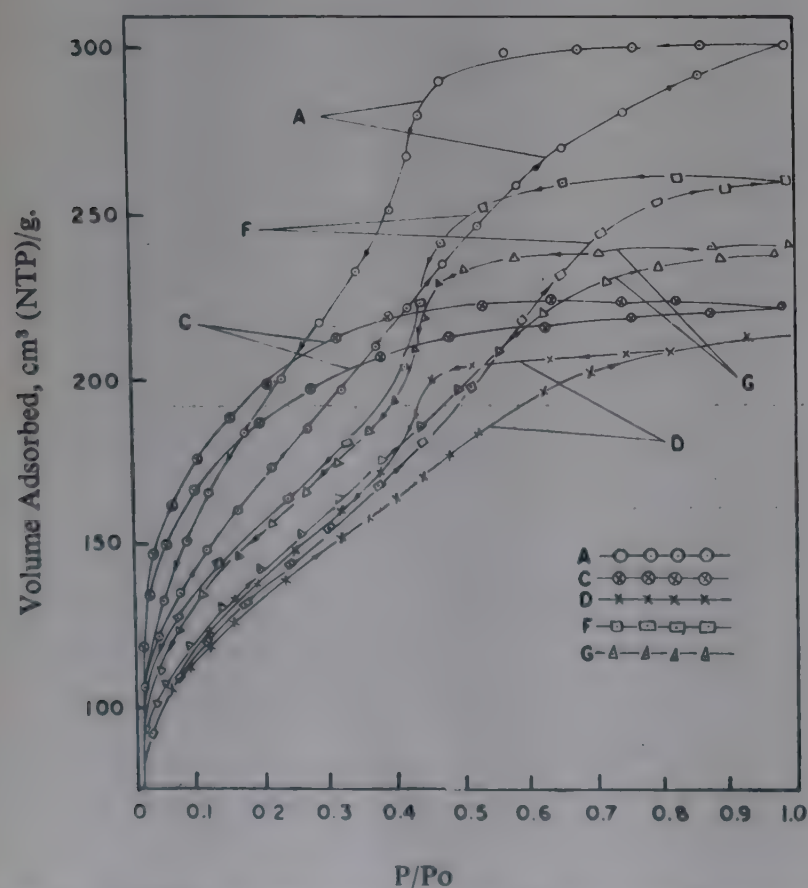


Fig. 1—Low Temperature Nitrogen Adsorption-Desorption Isotherms

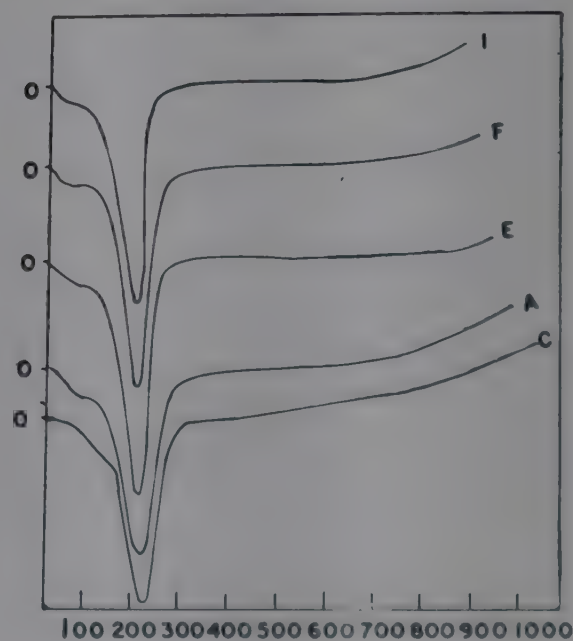
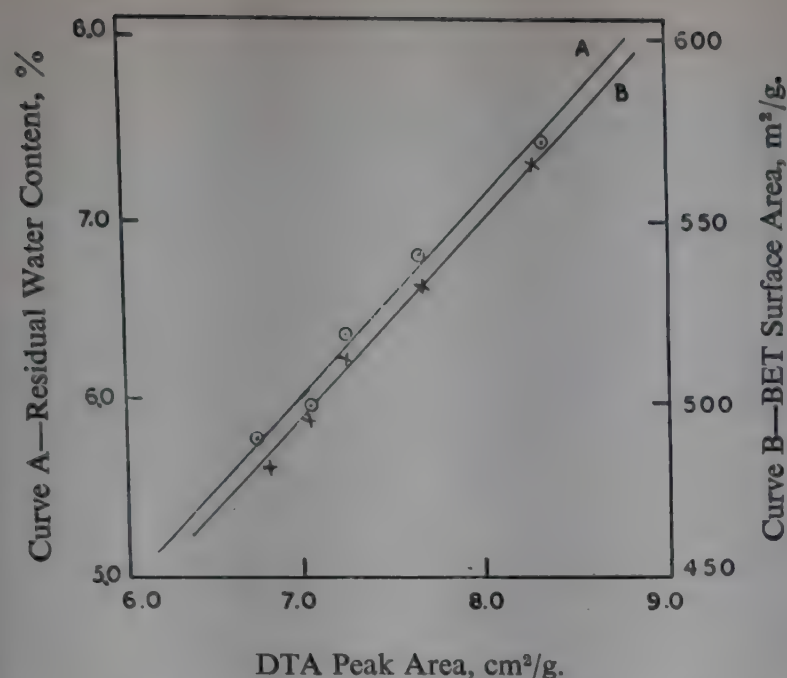


Fig. 2—DTA Thermograms

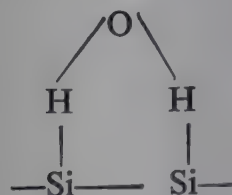


DTA Peak Area, cm²/g.

Fig. 3—Plot of BET Area and Percentage Residual Water Content against DTA Peak Area

Discussion

Sing and Madeley³ have observed that the pH of the final solution influences the setting time and the residual water content of the gel. They have found that setting times and residual water content decrease with the increasing pH of the final solution. They have also shown that temperature of gelation and time of ageing do not have any significant role in defining the gel structure. Adams and Voge⁴ by electron micrography studies on unaged silica-alumina gels showed that these gels consist of coherent aggregates of dense, smooth spherical particles, about 45 Å in diam. with relatively narrow distribution of particle sizes. Electron microscopy has also shown that the gelation of silica itself is essentially a polymerization-condensation reaction giving rise to surface of the following type.



This means that each silicon atom at the surface is associated with one hydroxyl group. Therefore, it should be possible to calculate the surface areas of the gels from the residual water content and molecular cross sectional area of water molecule given by Livingston⁵ (10.6 Å²), oriented on the surface as shown above or from the knowledge of the mean area available to the surface hydroxyl group, calculated indirectly from BET area and total number of surface hydroxyl groups.

The results of these two operations are shown in Table 2. The values, calculated by using cross-sectional area of water molecule, are much lower than the BET areas, which also confirms that the chemisorbed is not in the form of water molecules but as hydroxyl groups. The areas calculated on the basis of available area for each surface hydroxyl group (12.5 Å²) are very nearly of the order of BET areas. De Boer's⁶ values of residual water content have also been calculated for surface area taking 12.5 Å² as the cross-sectional area and the results are shown in Table 3.

The widely different nature of adsorption-desorption isotherms (Fig. 1) has little influence on the distribution of hydroxyl groups per unit area. DTA peak areas plotted against residual water content and surface areas showed a linear relationship.

In taking 12.5 Å² as the cross-sectional area of a hydroxyl group for calculating surface areas, one must recognize some other aspects of adsorbed hydroxyl groups. These adsorbed hydroxyl groups may be present in three different forms, free hydroxyl groups, hydrogen bonded hydroxyl groups, and hydroxyl groups which may be present in interstices of the ultimate gel particles. But assuming that bulk of the hydroxylation takes place as free hydroxyl groups on the surface, it may not

TABLE 3—DE BOER'S⁶ DATA OF RESIDUAL WATER CONTENT USED FOR RECALCULATING SURFACE AREAS ON THE BASIS OF AVAILABLE CROSS-SECTIONAL AREA FOR EACH HYDROXYL GROUP

Silica Sample	Residual Water Content (W), %	BET Area (S), m ² /g.	N _t (OH) × 10 ²¹	Surface Area 2 Using a 12.5 Å ² as Area Available to Each m ² /g.
Ethy 0	6.67	752	4.44	555.00
Ethy 1	5.17	475	3.44	430.00
Ethy 3	4.92	452	3.27	408.75
I Wa 0	7.19	697	4.79	598.75
I Wa 1	5.72	414	3.81	476.25
I Wa 2	6.91	710	4.60	575.00
2 Wa 0	3.16	324	2.10	262.50
2 Wa 1	3.46	297	2.30	287.50
3 Wa 2	4.77	462	3.17	396.25
4 Wa 3	2.77	192	1.84	230.00

be unjustified to take $12.5 \text{ \AA}^2$, for all practical purposes, as the cross-sectional area of a hydroxyl group for the calculation of surface area of silica.

Conclusion

It has been found from the present investigation that quick and fairly reliable surface areas of silica gels can be obtained from the determination of total surface hydroxyl groups.

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Changes on the physico-chemical and gas-solid chromatographic properties of silica gel upon salt-thermal treatment with different amounts of copper sulphate have been studied. A wide variation in the spectrum of gas chromatographic characteristics of these supports can be noted from their elution behaviour towards some isomeric C_6 hydrocarbons, the elution power increasing very rapidly in the range of 0 to 1 per cent copper content, followed by (i) no retention, in the range 1 to 2 per cent copper dosage (ii) gradually increasing retentive power thereafter and (iii) finally developing subtraction property for olefins and aromatics at copper levels higher than 8 per cent.

The cause of this drastic alternation in GSC behaviour of an adsorbent, thus modified, can be related with equally strong changes in the nature of adsorption sites, details of pore parameters and other physico-chemical properties. Results of cation-exchange power and exhaustive leaching with strong acid, positively indicate that silica gel binds copper from aqueous solutions of different strength by several distinct mechanisms. Follow-up studies by a combination of powerful instrumental techniques are expected to expose the much-needed mechanism of alteration of pore structure of adsorbents by salt-thermal treatment.

Mechanism of Alternation of Pore Structure of Silica Gel with Different Amounts of a Modifying Salt

By SAMIR K. GHOSH AND N. C. SAHA,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

The wide range of selectivity resulting from the salt coating of common adsorbents has been well exploited in gas-solid chromatography¹⁻¹⁵. Not much is, however, known about the physico-chemical changes on the adsorbents by the interaction of salts. For the first time, Saha *et al*¹⁶⁻¹⁸ have focussed the importance of this study in order to understand not only the retentive

mechanism of GSC and the technology of tailor-made adsorbents, but also the factors governing other common uses of adsorbents. In a series of publications,¹⁶⁻¹⁸ the various changes on the crystallo-chemistry, pore structure, nature of reactivity of the functional groups or atoms on the surface, the gradual swelling of micro-crystallites into big globules have been demonstrated

with a few common adsorbents and with different modifying salts.

Mougey, *et al*¹⁹ have demonstrated that silica gel containing different amounts of adsorbed cations like Na⁺, K⁺ and Ca²⁺, when subjected to dehydrating treatments upto 400°C undergo significant textural changes, viz. changes in surface area, pore volume and pore size distribution. The purpose of the present study is to investigate some of the physico-chemical changes and their effects on the GSC properties of silica gel when it is modified with varying amounts of copper sulphate.

Experimental

An Aerograph 600D model gas chromatograph with FID and argon-carrier was used. The method of coating and calcining silica gel with copper sulphate has been described earlier. The salt-treated adsorbent was packed into either 5' or 10' copper tubing of about 2 mm. bore by the conventional method and gas chromatographic properties determined for silica gels containing varying amounts of copper.

In a second series of experiments, 5 ml. of silica gel activated at 200°C in air for 2 hr. was treated with 50 ml. of copper sulphate solutions of different concentrations and allowed to equilibrate for 45 min at the ambient temperature. The coating solution was then filtered in a small Gooch crucible, but the residue was not washed with water. pH of the initial and final coating solutions was determined with a Beckman expanded scale pH meter and the difference was noted as Δ pH. The amount of copper retained on silica was calculated from the difference in copper sulphate concentration of the coating solution before and after treatment of the silica gel.

In the third series, the salt-thermal modified silica supports were leached several times with 6N hydrochloric acid at room temperature till copper was found absent in the washing. The amount of copper dissolved out in hydrochloric acid was determined iodometrically.

Finally the apparent densities of the silica supports containing different amounts of copper were compared by packing them identically (as far as possible) in a glass tube 5.4 cms. $\times$ 5.3 mm. of capacity 1.2 ml.

Results and Discussion

(a) *Selectivity towards Isomeric C₆-Hydrocarbons:* Retention behaviours of normal hexane, cyclohexane, hexene-2 and benzene were expected to reveal some significant features because of their difference in the distribution of electron density and geometric configuration. It was found that none of these solutes are eluted from blank silica at 170°C. Elution of n-hexane begins

at a very low content of copper on silica, then rises very rapidly till the stage of no retention is reached at about 1 per cent copper on silica. Thereafter, retention volume increases regularly with large dosage of copper. This phenomenon can be explained on the basis of average pore diameter which is the only major parameter controlling the retentive mechanism of normal paraffins on adsorbents. Compared with n-hexane, cyclohexane exhibits a peculiarity, namely there is a critical concentration of copper around 4.4 per cent below which cyclohexane has higher retention than n-hexane, but above which it has a lower retention. Evidences are there that cyclohexane can elute earlier²⁰ or later¹⁶ than n-hexene depending on the nature of adsorbents and their modifications. There is, however, no precise information about the support parameters which cause this type of differential behaviour.

From a 0.2 per cent Cu-SiO₂ column at 170°C hexane-2 is not eluted, but benzene is eluted with a specific retention volume of 2.013 ml. Thereafter, with increasing copper dosage, elutions of both hexane-2 and benzene increase very rapidly, both having little, or no retention around 1.0 to 2.0 per cent copper on silica. Inference has, therefore, been drawn that the modified silica support containing 1 to 2 per cent copper is completely inert with respect to the availability of pores towards the C₆ hydrocarbons and also with respect to the pi-bonding capacity towards olefins and aromatics. Silica, containing more than 2 per cent copper, again develops retention power for both saturated and unsaturated hydrocarbons. The retentive mechanism for the saturates can be explained through creation of new pores, and for the unsaturates possibly through interaction with copper (Table 1). Silica support with 4 per cent copper yielded very sharp and symmetric peaks for both hexane and benzene. Peak tailing which is an indication of partial elution and

TABLE 1—CHANGES IN THE PHYSICAL PROPERTIES OF SILICA BY SALT MODIFICATION

Copper on Silica, w/w %	Surface Area, m ² /g	Pore Volume, ml./g.	Apparent Density, g./ml.
—	375.0	0.480	0.593
0.2	32.7	0.096	1.225
1.06	<1.0	0.026	1.489
2.0	<1.0	0.023	1.474
4.38	—	—	1.472
8.06	—	—	0.911
11.7	24.0	0.477	0.781

partial adsorption by the support, starts around 8 per cent copper. At 170°C benzene was absorbed completely by 11 per cent copper on silica, while hexene required somewhat lower dosage of copper. The difference in the retentive power of silica containing different amounts of copper for hexene-2 and benzene can also be noted clearly from Fig. 1. This figure shows that (a) pi-bonding capacity of silanols for aromatic double bonds are more strongly affected by copper than for olefinic unsaturation, and (b) the interaction of copper with aromatics is relatively weaker than that with olefins of comparable molecular dimensions.

(b) *Modes of Attachment of Copper on Silica:* French and Howard²¹ have demonstrated that the hydroxyls of silica gel undergo cation-exchange with aqueous copper sulphate, the sulphate ion not being exchanged at all. Obviously, the change in pH of the copper sulphate solution is by cation-exchange only. It has been observed in our laboratory that when a given weight of silica gel is treated with a fixed volume of aqueous copper sulphate solutions of different concentration, there is a significant variation in the pH of the coating solution (Table-2). Mention may be made that the change in pH was complete within 20 min. in each case and even after 24 hr. of treatment further change was not noticed. Fig. 2 reveals a rapid increase in the amounts of cation-exchange in

TABLE 2—CHANGES IN THE pH OF COPPER SULPHATE SOLUTIONS OF DIFFERENT STRENGTH WHEN EQUILIBRATED WITH SILICA

Copper Retained on Silica, w/w %	pH of the Coating Solution	
	Before Treatment	After Treatment
0	6.06	4.35
0.2	4.80	3.33
1.0	4.58	3.50
2.0	4.42	3.60
4.0	4.23	3.63
8.0	4.00	3.65

the range 0-3 per cent copper, and for solutions containing above 8 per cent salt the pH practically remains constant. The increase in the base-exchange power of silica gel with rise in the concentration of salt is not clearly understood. Presence of increasing amounts of salt, either adsorbed or in the aqueous solution, might be responsible for releasing hydroxyl ions from the bulk to the surface of silica gel, or converting potential and bound silanols to exchangeable hydroxyls.

The significant variation in the amount of copper sulphate retained on silica by exhaustive leaching with hydrochloric acid is also indicative of a difference in the mode of attachment of salt. Undoubtedly, unbound salt is completely removed by the acid treatment and hence, in absence of a difference in the retentive mechanism of copper sulphate, the amount of metal finally held on the silica gel should have been constant irrespective of the salt concentration of initial coating solutions.

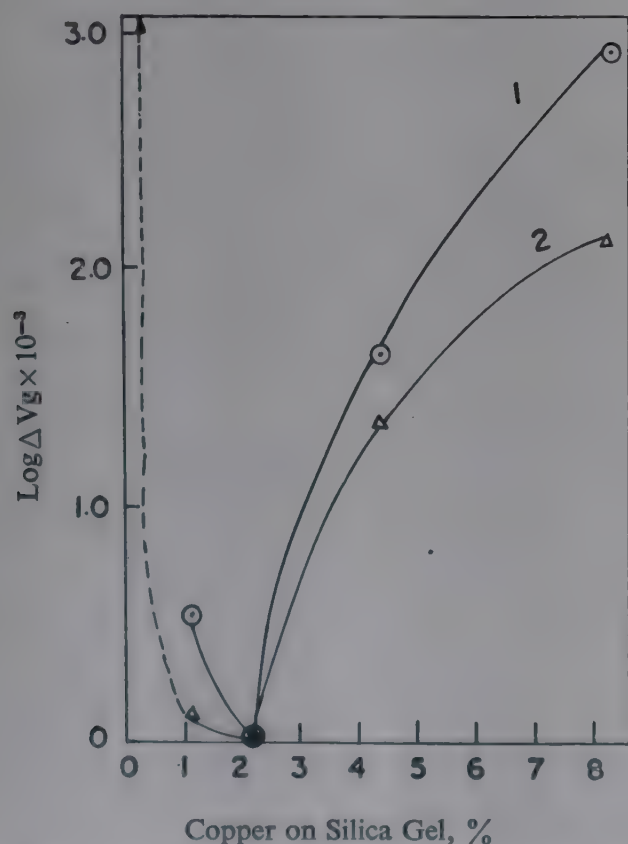


Fig. 1—Variation of π -Bonding Capacity of Silica Support for Aromatic and Olefinic Double Bonds with the Amount of Modifying Agent

1. Vg Hexane 2-Vg n-Hexane:
2. Vg Benzene-Vg n-Hexane

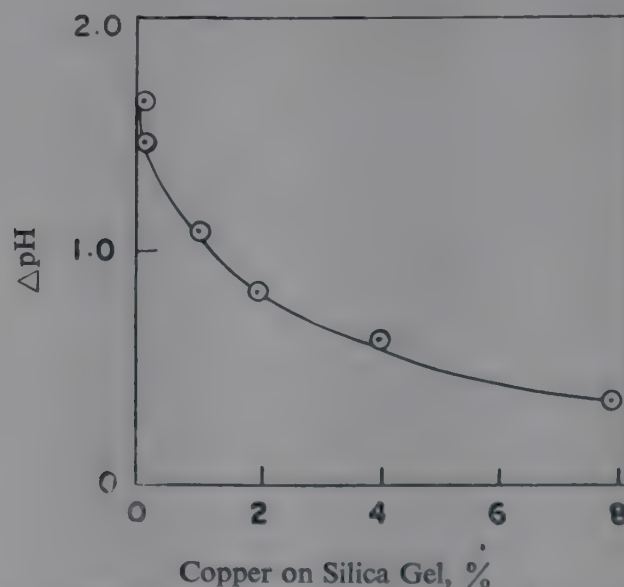


Fig. 2—Effect of Percentage of Modifying Salt upon pH of Silica Support

TABLE 3—MODES OF ATTACHMENT OF COPPER BY SILICA GEL

Copper on Silica, w/w %	
Before Leaching	After Leaching
1.06	1.06
2.13	1.874
4.38	3.981
8.20	3.240

Further research is needed to throw light on the mechanism of this differential adsorption behaviour and final retention of copper. From the big change in the spectrum of GSC properties of salt-modified silicas as already discussed, it is obvious that support parameters are drastically altered when silica gel containing different amounts of copper sulphate are calcined to 950°C. This is also supported by the results in Table 1. Surface area and pore volume of silica fall very rapidly with small dosage of copper sulphate so that at 1.0 to 2.0 per cent level of copper the support has lost completely the original pore structure of silica gel. This explains the complete loss of selectivity and retentivity of the silica support containing 1-2 per cent copper. It can be noted that at this range the support has maximum density. The wide variation in the apparent densities of silica-supports (vide last column in Table 1) might be due to difference in the size distribution of either particles or globules or both. At higher dosage of copper sulphate the mechanism of regeneration and creation of pores, as already elaborated,¹⁶⁻¹⁸ starts with silica. Detailed study with a number of instrumental techniques is under progress to follow the courses of alteration of pore structure of silica gel with different amounts of salt-coating as well as the implications on gas chromatographic properties of the resultant supports.

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Infrared absorption studies have been carried out with sodium polymetaphosphate mixed with varying amounts of sodium sulphate. The characteristic bands of cyclic phosphates have been observed in presence of sodium sulphate. Sodium sulphate has been found to catalyze the formation of cyclic phosphate. Sodium polymetaphosphates with $\text{SO}_3/\text{P}_2\text{O}_5$ ratio upto 0.20 are found to be of transparent nature due to solubility of sodium sulphate in sodium polyphosphate. Supersaturation took place above $\text{SO}_3/\text{P}_2\text{O}_5$ ratio > 0.2 , resulting in the formation of opaque solids.

Infrared Absorption Studies on $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{SO}_3$ System: Part 2

By R. M. BHATNAGAR, R. M. VERMA, A. K. CHAKRAVORTY
AND A. K. ROY,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

In a previous communication¹, the presence of all characteristic bands of linear and cyclic phosphates were identified by an infrared absorption study in a commercial sodium polyphosphate as well as sodium polyphosphate with high sodium sulphate content which is being produced in this laboratory². Various absorption bands were characterized and compared with other commercial polyphosphates.

In the present investigation, the system was further studied by infrared absorption analysis of glasses containing sodium polyphosphate and sodium sulphate in various ratios.

Experimental

Method: Infrared absorption studies of sulphated polyphosphate samples having different sulphate polyphosphate ratios in the solid phase were carried out by potassium bromide disc technique using Perkin-Elmer infrared dual grating spectrophotometer (Model 421). The technique for the preparation of potassium bromide pellet is the same as reported earlier¹.

Materials: Sodium polyphosphate sample was prepared by heating analar sodium dihydrogen orthophosphate in a furnace at 650°C . The molten mass, thus obtained, was quenched on ice-cooled stainless steel plates. Sulphated sodium polyphosphate samples were prepared by heating a suitable mixture of above sodium

polyphosphate and anhydrous sodium sulphate at 850°C and quenching as above. The samples with various molar ratios of sodium polyphosphate and sodium sulphate were prepared.

The phosphorus pentoxide and sulphur trioxide contents of the glasses were determined, after hydrolysis with nitric acid by the methods described earlier¹. The end-group or number average molecular weights of the samples were determined by pH titrations³.

Results and Discussion

The condition of formation, end-group molecular weights and the nature of the sodium polyphosphate samples admixed with varying amounts of sodium sulphate are presented in Table 1. The samples of such polyphosphates are characterized by their $\text{SO}_3/\text{P}_2\text{O}_5$ ratio in the present work. It has been observed that samples upto $\text{SO}_3/\text{P}_2\text{O}_5$ ratio equal to 0.20 are transparent glasses while above this ratio they are white opaque solids. Their end-group molecular weights are found to decrease with increasing $\text{SO}_3/\text{P}_2\text{O}_5$ ratio.

Infrared spectra of the sodium polyphosphate samples with $\text{SO}_3/\text{P}_2\text{O}_5$ ratio 0.086 to 0.98 (samples 2 to 4) together with pure synthetic sodium polyphosphate and anhydrous sodium sulphate are presented in Fig. 1. The assignments have been made according to Corbridge and Lowe^{1,5}.

The weak band at $1640\text{--}1610\text{ cm}^{-1}$, which is present in

TABLE 1—COMPOSITION, CONDITIONS OF FORMATION, END GROUP MOLECULAR WEIGHT AND NATURE OF SODIUM POLYPHOSPHATE SAMPLES ADMIXED WITH SODIUM SULPHATE

(Time of heating: 2 hr.)

Sample No.	Composition of Heating Mixture	Temperature, °C	% P_2O_5	% SO_3	Ratio of SO_3/P_2O_5	End Group Molecular Weight	Nature
1.	Sodium dihydrogen orthophosphate alone	700±10	69.1	—	—	8,380	Transparent glass
2.	Sodium polyphosphate (6 moles + sodium sulphate (1 mole)	850±10	63.1	5.4	0.086	3,600	Transparent
3.	Sodium polyphosphate (4 moles) + sodium sulphate (1 mole)	„	55.8	11.0	0.20	2,860	Transparent
4.	Sodium polyphosphate (3 moles) + sodium sulphate (1 mole)	„	52.9	13.9	0.26	2,677	White turbide
5.	Sodium polyphosphate (2 moles) + sodium sulphate (1 mole)	„	44.7	21.3	0.48	2,615	White opaque
6.	Sodium polyphosphate (1 mole) + sodium sulphate (1 mole)	„	33.0	32.0	0.98	2,605	White opaque

almost all the samples of polyphosphates, is the OH bonding mode of either water of crystallization in the sample or due to absorption of moisture during potassium bromide pellet preparation.

Sample 1 of pure sodium polyphosphate (curve 2, Fig. 1) shows very strong and broad bands near 1270 and 865 cm^{-1} , which are characteristics of linear metaphosphates. Two other broad bands at 1083 cm^{-1} (strong) and 980 cm^{-1} (medium) along with weak bands at 1150(sh), 770(broad) and 700(broad) appear in the spectrum which agree with data obtained by Corbridge and Lowe for sodium metaphosphate $(NaPO_3)_n$ (glass). The spectra show complete absence of any cyclic phosphate.

With addition of sodium sulphate three strong and sharp bands at 1312, 1295 and 1258 cm^{-1} along with a very strong band near 990 cm^{-1} appear in all the samples (samples 2 to 6, curves 3 to 7, Fig. 1); these bands are characteristic of cyclic metaphosphates. The other bands of cyclic metaphosphate like a strong doublet at 773 and 753 cm^{-1} and two medium and weak bands at 687 and 668 cm^{-1} respectively also appear in all these spectra. However, the features in the region 900-1270 cm^{-1} change with increasing SO_3/P_2O_5 ratio. In sample 2 (curve 3, Fig. 1), where SO_3/P_2O_5 is lowest viz. 0.09, the 1000-1260 cm^{-1} region shows bands at 1167(s), 1120(s), 1102(vs), 990(vs, br) which compares well with the values of sodium trimetaphosphate as given by Corbridge and Lowe.

As sodium sulphate concentration is increased in samples 2 to 6 (curves 3 to 7, Fig. 1), the very strong and broad band near 1120 cm^{-1} of sulphate ions is superimposed over the other bands and masks the region, thereby creating difficulty in identifying the individual bands particularly in sample 6 (curve 7, Fig. 1), where sodium sulphate concentration is very high. Therefore, a run was taken by putting a little sodium sulphate in reference beam, and sample 6 was placed in sample beam, so as to reduce sodium sulphate interference (Fig. 2). On scrutiny, it is seen that the spectrum, apart from showing bands of sodium trimetaphosphate, also shows bands at 1214(s), 1184(sh, s), 1165(vs), 1145(sh,s), 1098(s), 1016(sh,w), 906(vs,-b), 737(m,sh) 665(s), which are known to be due to sodium triphosphate-II. Careful observation reveals the presence of sodium triphosphate-II also in samples 2 to 5. As sodium sulphate content increase from samples 2 to 6, more and more sodium triphosphate is formed which is apparent by the increase of intensity of the chain phosphate bands at 906 and 665 cm^{-1} .

The following interesting feature may be mentioned here: At higher sodium sulphate concentration, the $(SO_4)^{-2}$ ion bands at 635 and 625 cm^{-1} also mask two weak bands at 625 and 602 cm^{-1} ; this may be due to ionic orthophosphates formation. Another band of ionic orthophosphate at 570 cm^{-1} is also noticed in increasing intensity from samples 2 to 6 (curves 3 to 6, Fig. 1).

It may be inferred from infrared absorption studies

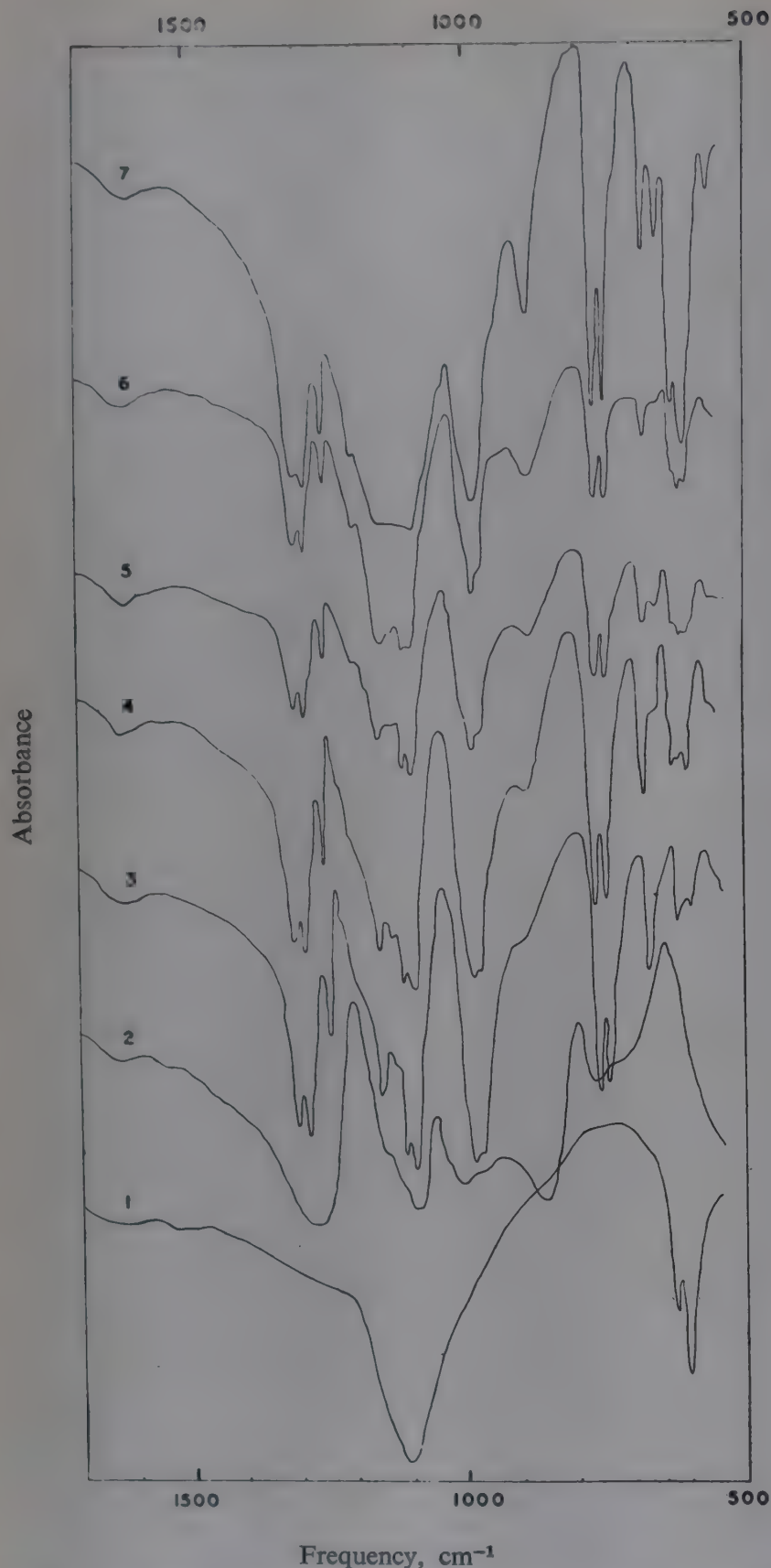


Fig. 1—Infrared Absorption Spectra of Sodium Polyphosphate and its Mixture with Sodium Sulphate
Curve 1—Sodium Sulphate (Anhydrous)
Curve 2—Sodium Polyphosphate (Pure)
Curves 3-7—Sulphated Sodium Polyphosphate

that chain phosphates are converted to cyclic phosphates in the presence of sodium sulphate, which may act as a catalyst. The SO_4^{2-} ion at higher concentration does not react with polyphosphate and remains as such. Ohashi and Ikeda- also carried out x-ray studies of the reaction of sodium polymetaphosphate with disodium sulphate at higher temperature and could not confirm the pre-

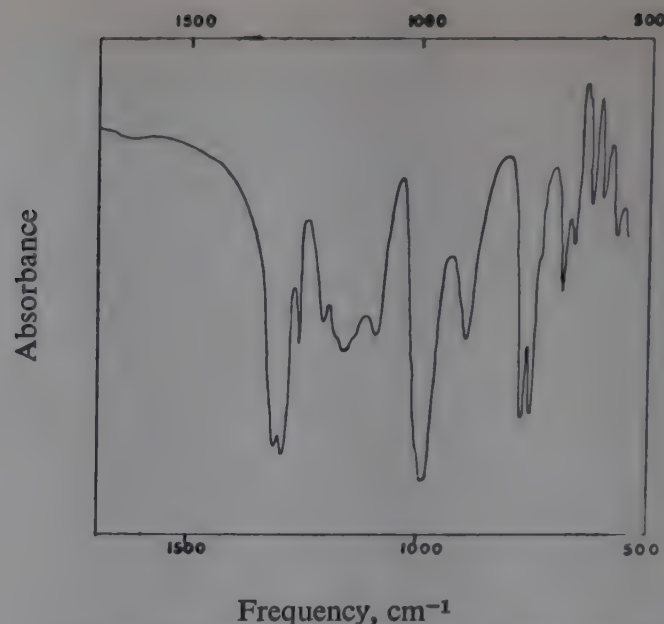


Fig. 2—Sample VI with Sodium Sulphate in Reference Beam

sence of S-O-P linkage as a major component in the crystalline substance as reported by Poni and Carnatescu⁷. The infrared absorption spectra of transparent glasses (samples 2 and 3) could not reveal any structural difference when compared with the opaque samples (samples 4 to 6), except the formation of sodium tri-polyphosphate at higher $\text{SO}_3/\text{P}_2\text{O}_5$ ratio. Formation of cyclic and chain phosphates depends on $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$ ratio. The gradual increase in sodium sulphate, content of sodium polyphosphate changes the $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$ ratio, which results in the formation of cyclic and chain phosphates. The transparent nature can be explained as due to solubility of sodium sulphate in sodium polymetaphosphates resulting in the formation of solid solutions; supersaturation of sodium sulphate takes place at $\text{SO}_3/\text{P}_2\text{O}_5$ ratio above 0.20, with the formation of white opaque solids.

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Decomposition of ammonium nitrate with and without additives has been studied thermogravimetrically at 225° and 245°C. pH of the residues has been determined. Urea, zinc oxide and their mixture have been found to be effective as inhibitors at both the temperatures. Explosivity of some of the samples has been determined. A maximum increase in the explosion temperature of ammonium nitrate was recorded with zinc oxide as an additive. The results are discussed.

Influence of Additives on the Hazardous Behaviour of Ammonium Nitrate

By S. VARMA AND R. C. SAXENA,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

The study of the thermal decomposition of ammonium nitrate and the influence of various additives on the extent of decomposition of the salt is important in the context of the hazards associated with the handling and storage of ammonium nitrate as well as the nutrient loss occurring during the production and storage of mixed fertilizers, in which ammonium nitrate is present as one of the components. The strong catalytic influence of chloride ion on the decomposition of ammonium nitrate is well-known¹⁻⁵. Recently, Parker and Watchorn⁶ have shown that the presence of chloride ion causes self-sustained decomposition even in mixed fertilizers containing ammonium nitrate as one of its components.

Ammonium nitrate under unconfined conditions dissociates into ammonia and nitric acid, soon after, it melts at 169°C and starts evolving nitrous oxide and water. The former reaction is highly endothermic and the latter is weakly exothermic. As a result of these two concurrent reactions, the ammonium nitrate melt tends to reach a steady temperature and there is little tendency towards self-accelerating decomposition or even continued reaction after the source of heat is removed^{7,8}. The situation changes when ammonium nitrate decomposes under confined conditions. It has been stated that for explosive decomposition of pure ammonium nitrate by thermal means, it is necessary to have existence of confinement which allows the product gases to develop a pressure of 100 kg./sq. cm. and the temperature around 300°C^{9,10}.

Desensitizing influence of urea on the thermal decomposition of ammonium nitrate has been studied by

various workers^{11,12}. Rosebourne and Findlay¹³ were first to demonstrate thermogravimetrically that the presence of small amounts of urea inhibited the thermal decomposition of ammonium nitrate. Veley¹⁴ and others^{15,16} reported that decomposition of ammonium nitrate melt could be prevented by keeping it alkaline by bubbling ammonia. Recently, Mandany and Burent¹⁷ have studied thermogravimetrically the effect of halides of potassium and ammonium at 225°C and found that potassium bromide and iodide are the most effective inhibitors. A free radical mechanism was proposed by the same authors to explain the desensitizing influence of bromide and iodide of potassium. Rozman¹⁸ found that zinc oxide present in small amounts also inhibited the decomposition of ammonium nitrate.

In the previous communication¹⁹ it was found that when ammonium nitrate was heated at a constant rate, the gases evolved continued to be alkaline upto 245°C after which they became acidic. Urea and zinc oxide, when present to the extent 2 per cent in ammonium nitrate, increased this transition temperature to 270°C whereas calcium carbonate increases it to 250°C. The extent of the increase of this temperature was considered to provide a reliable index for the effectiveness of an additive as an inhibitor.

A question arises whether these additives which inhibit the decomposition of ammonium nitrate do in fact desensitize the salt and reduce the explosion hazard, since thermogravimetric studies are carried out in open system whereas ammonium nitrate is known to explode only under confinement.

Experimental

Procedure: All the chemicals used were of analytical grade. The thermal decomposition of ammonium nitrate was studied thermogravimetrically at 225 and 245°C. An accurately weighed amount (10g.) of perfectly dry ammonium nitrate—dried over sulphuric acid in a desiccator and 2 per cent by weight of additive were mixed thoroughly prior to transferring into a weighed tube, which was placed in a larger tube and corked properly. A vent and thermometer were fitted into the cork. The entire assembly was placed in an oil-bath maintained at the desired temperature, after 4 hours of heating the entire assembly was taken out of the oil-bath, the smaller tube removed and cooled in a sulphuric acid desiccator and weighed accurately. The total loss in weight was calculated from the decrease in weight of the sample in each case. The change in acidity was determined by measuring the pH of 8 per cent solution of the residue. The explosion temperature of pure ammonium nitrate and some of its sample with various additives was determined by the method followed by Varma and Sinha²⁰.

Results and Discussion

A close relationship is stated to exist between the acidity of the melt and the rate of decomposition of ammonium nitrate and it has been found that the additives which increase the pH of the melt inhibited the

decomposition of ammonium nitrate¹¹. Mandany and Burnet¹⁷ showed that the decomposition of ammonium nitrate was inhibited by the addition of buffers to control the acidity of the melt. In the present series of experiments, pH of the residues has been determined at two temperatures, viz. 225 and 245°C. The results (Table 1) indicate that there is no significant difference in the pH of the residues of various samples examined at the two temperatures except that some of the additives increased pH only at 225°C and the lowest pH recorded is around 3. This is understandable as the dissociation of ammonium nitrate into ammonia and nitric acid reaches an equilibrium when dissociation and neutralization proceed at an equal rate:



When the samples contained urea, zinc oxide or their mixture as additives, the pH of the residue was consistently on the higher side, i.e. around six or more at both the temperatures at which thermogravimetric studies were made. Di- and tricalcium phosphate increased the pH of the residue by about two units at 225°C but no significant change was observed at 245°C. Likewise, potassium iodide, calcium carbonate and ammonium oxalate increased the pH of residues obtained at 225°C but not at 245°C. Slight lowering of pH was observed in the case of ammonium phosphates at both the temperatures.

TABLE 1

Samples	Weight-loss in 10 g. of Ammonium Nitrate Heated for 4 hr, g.		pH of 8 per cent Solution of the Residue at Two Temperatures	
	225°C	245°C	225°C	245°C
Ammonium Nitrate	0.87	4.36	3.2	3.1
Ammonium Nitrate + 2% CaHPO ₄	0.48	6.06	5.3	3.2
Ammonium Nitrate + 2% (NH ₄) ₂ HPO ₄	0.56	5.90	2.8	2.7
Ammonium Nitrate + 2% Ca(H ₂ PO ₄) ₂	1.15	6.47	3.1	3.1
Ammonium Nitrate + 1% CaHPO ₄ + 1% CO(NH ₂) ₂	0.46	5.73	3.8	3.5
Ammonium Nitrate + 1% CaHPO ₄ + 1% (NH ₄) ₂ C ₂ O ₄	0.36	5.50	5.3	3.3
Ammonium Nitrate + 2% NH ₄ H ₂ PO ₄	0.91	6.05	2.5	2.4
Ammonium Nitrate + 2% Ca ₃ (PO ₄) ₂	0.36	5.33	5.6	3.2
Ammonium Nitrate + 2% KI	0.25	3.87	5.0	3.5
Ammonium Nitrate + 2% CaCO ₃	0.48	3.01	4.0	3.3
Ammonium Nitrate + 2% (NH ₄) ₂ C ₂ O ₄	0.24	2.44	4.6	3.1
Ammonium Nitrate + 1% (NH ₄) ₂ C ₂ O ₄ + 1% CO(NH ₂) ₂	0.19	1.67	5.9	3.1
Ammonium Nitrate + 2% ZnO	0.16	1.40	7.1	6.8
Ammonium Nitrate + 1% ZnO + 1% (NH ₄) ₂ C ₂ O ₄	0.18	1.18	7.0	6.7
Ammonium Nitrate + 1% ZnO + 1% CO(NH ₂) ₂	0.16	0.61	7.0	6.9
Ammonium Nitrate + 2% CO(NH ₂) ₂	0.18	0.35	5.8	5.9

The relationship between the pH of the melt and the extent of weight-loss are observed strikingly in the case of additives, such as zinc oxide, urea and their mixture, where the inhibition of the thermal decomposition is more when the pH is high. In the case of other additives, the results do not appear to conform to the expected pattern specially when the pH of the melt is not significantly different from that of the pure ammonium nitrate. This is not surprising since the equilibrium of the reversible reaction (eqn.1) is likely to be shifted in presence of additives, changing thereby the equilibrium concentration of free nitric acid of the melt. From the results in Table 2, it is clear that zinc oxide is the most

TABLE 2

Samples	Explosion Temperatures (E _T), °C
Ammonium Nitrate	283
Ammonium Nitrate + 2% ZnO	340
Ammonium Nitrate + 2% Urea	333
Ammonium Nitrate + 2% DAP	330
Ammonium Nitrate + 2% CaCO ₃	312
Ammonium Nitrate + 2% MAP	305
Ammonium Nitrate + 2% Ca(H ₂ PO ₄) ₂	294
Ammonium Nitrate + 2% CaHPO ₄	288
Ammonium Nitrate + 2% Ca ₃ (PO ₄) ₂	285

effective inhibitor and that urea and diammonium phosphate rank next and both are equally effective. The 3°C difference in the explosion temperature represents a very small difference in the effectiveness of the two additives*. Rozman^{21,22} stated that the effectiveness of an additive as an inhibitor depended on their ability to liberate ammonia slowly. Both zinc oxide and urea have this property. Urea hydrolyses to liberate ammonia and zinc oxide reacts with ammonium nitrate to form zinc ammine complex which liberates ammonia slowly when heated above 200°C.

The explosion test results in Table 2 indicate that the effectiveness of the additives increasing the explosion temperature (desensitization) decrease in the following order: zinc oxide > urea ~ diammonium phosphate >

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calcium carbonate. All these substances liberate ammonia. Braconier and Delsemme¹⁰ found that substances liberating or aiding the liberation of ammonia increased the explosion temperature. Among the non-ammonia liberating substances, mono-ammonium phosphate, mono-, di- and tricalcium phosphates also increase, though to a lesser extent, the explosion temperature of ammonium nitrate. The effectiveness of a desensitizer does not appear to be solely dependent on their ability to evolve ammonia slowly. Diammonium phosphate and calcium carbonate, when heated along with ammonium nitrate, tend to evolve ammonia at a relatively lower temperature than urea and zinc ammine nitrates. Yet these additives also prove effective in increasing the explosion temperature. It may well be that concentration of ammonia in the gaseous phase in a confined system may influence the progress of reaction, which in due course becomes self-accelerating and leads ultimately to the explosive decomposition of the salt. An increase in the partial pressure of ammonia in the gaseous phase may inhibit the decomposition of ammonium nitrate by suppressing the dissociation reaction or under certain conditions of confinement may aid the system to become self-accelerating by controlled suppression of endothermic dissociation. The latter appears to cause lowering of the explosion temperature of ammonium nitrate containing desensitizers, such as urea and calcium carbonate, when the confinement volume is increased whereas in the case of pure ammonium nitrate it is just the reverse²⁰.

It may, therefore, be stated that a correct choice of a desensitizer can only be made by carrying out explosion tests. It is fallacious to assume that ammonia-liberating substances under all conditions stabilize ammonium nitrate. Thermogravimetric studies at best reveals only the effectiveness of an additive as an inhibitor of the thermal decomposition of ammonium nitrate which may or may not prove effective as a desensitizer.

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The cation-exchange equilibria of cation-exchange resin prepared from waste acid sludge have been studied for different uni-univalent and uni-divalent systems. In the monovalent series, the order of affinity of hydrogen form exchanger for various cations has been found to be in the following order: lithium < sodium < potassium = ammonium < silver; and in divalent series the affinity for cations can be represented in the following order: magnesium < cobalt < manganese < nickel < copper < calcium < barium.

Further, the effects of temperature and particle size of resin upon exchange equilibrium have also been studied; the increase in equilibrium constant has been observed with the increase in temperature and also by decrease in particle size of resin.

Studies on Cation-Exchange Resin from Acid Sludge: Cation Exchange Equilibrium

By B. K. DUTTA AND V. K. SETH,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

Various literature on exchange of different pairs of ions with different valencies show that the distribution coefficient varies appreciably with concentration, composition of solution and with the properties of interchanging ions and resin¹⁻⁵. Most of the fundamental studies on ion-exchange equilibria have been carried out with relatively simple systems so that the basic principles may easily be understood. If the complicating effects, such as those due to formation of complexes in solution, are absent, the distribution of exchanging ion between resin and solution is determined by their concentration in resin and solution phases.

The equilibrium for five different types of ion-exchange resins in hydrogen form was studied by Bhatnagar⁶ over a wide range of exchanging ions in external solution. Further results showed that for all cases the apparent equilibrium quotient K_a varied irregularly with concentration of external solution and so with equivalent fraction of ion in resin phase i.e. X_R . Bonner⁷ studied the equilibrium of cation-exchange resin in different forms, with various uni- and divalent cations and obtained thermodynamic equilibrium constants. Govindan^{8,9} has studied exchange equilibria of cashew nut shell liquid resin on the basis of law of mass action, and established that in a stronger solution resin is more selective to

monovalent cations, while in a comparatively dilute solution, it favours divalent cations.

The details of derivation of equilibrium quotient for univalent and uni-divalent systems based on law of mass action have already been reported¹⁰. Further refinements were made by Davidson¹¹ by taking into account the activity coefficient in resin phase. They employed the following equation to determine equilibrium constant K, derived by law of mass action and Gibbs-Duhem equation.

$$\text{Log } K = \int_{X_R = 0}^{X_R = 1} \text{Log } K_a \, dX_R \tag{1}$$

where K_a is equilibrium quotient which can be expressed for uni-univalent system.

$$K_a = \frac{X_R (1 - X_s)}{X_s (1 - X_R)} \tag{2}$$

and for uni-divalent system

$$K_a = \frac{C_o}{P_a Q} \frac{X_R (1 X_s)^2}{X_s (1 - X_R)^2} \tag{3}$$

X_R is ionic fraction in resin phase, X_s ionic fraction in solution phase, C_o the total concentration of cation in solution phase in meq./ml., Q the total exchangeable ions present in resin phase in meq./g. and P_a is apparent density of exchanger in dry hydrogen form in g./ml. The integration of equation (1) may readily be carried out for finding the value of K on plot of K_a vs X_R .

In the present investigation, the cation-exchange equilibria of cation-exchanger, Sindex—C 26, prepared in this laboratory from acid sludge¹²⁻¹⁴ with active sulphonic acid group in hydrogen form, has been taken for consideration with other uni - and divalent ions and the equations (1), (2) and (3) were used for calculating the values of equilibrium constant K . The effects of particle size of resin and of temperature upon equilibrium constant were also studied.

Experimental

Materials: The cation-exchange resin, Sindex—C26, after soaking completely with water was crushed and sieved to a particular desired size. The detailed analysis of resin is given in Table 1. The sieved resin was then taken in a glass column in a manner that no air bubbles were trapped between the particles. 1N hydrochloric acid was allowed to flow downwards through the resin column at a slow rate until acidity of effluent comes the same as of influent. Resin was then washed with water to remove the excess acid adsorbed on the surface of resin.

TABLE 1—CHARACTERISTICS OF RESIN SAMPLE (Sindex-C 26)

(i) Strong Acid Capacity	..	0.655 meq./ml. 1.395 meq./g.
(ii) Bulk Density	..	0.46 g./ml.
(iii) Total exchange capacity	..	1.09 meq./ml. 3.16 meq./g.
(iv) Swelling (H ⁺ form)	..	60.7%

In order to minimize any possible changes in its physical structure the resin was air-dried at room temperature, the residual moisture content of resin varied from 10 to 25 per cent.

Analytically pure or high grade (C.P.) chemicals were used throughout the experiment. All the solutions used were standardized by the normal procedure.

Method: The moisture content of air-dried resin in hydrogen form was determined by drying a weighed quantity of resin sample to a constant weight at 105-110°C. Samples (about 1 g.) of air-dried resin were weighed accurately and transferred to 200 ml. air-tight glass stoppered bottles. Different volumes of accurately measured 0.1N solution of metallic salts were added to the bottles and the volume was adjusted to 100 ml. by adding 0.1N hydrochloric acid except in case of $H^+ = Ag^+$ equilibrium where 0.1N nitric acid was used. It has been established earlier, in case of hydrogen-form exchanger with sodium chloride solution in liquid phase, that the equilibrium is over within 1 hr. (as can be seen in Fig. 1); so the time for attainment of equilibrium with all the salts was kept for about 24 hr. The solutions were then decanted from the bottles and an aliquot portion of solution was drawn for determination of the acidity generated due to exchange of cations with hydrogen

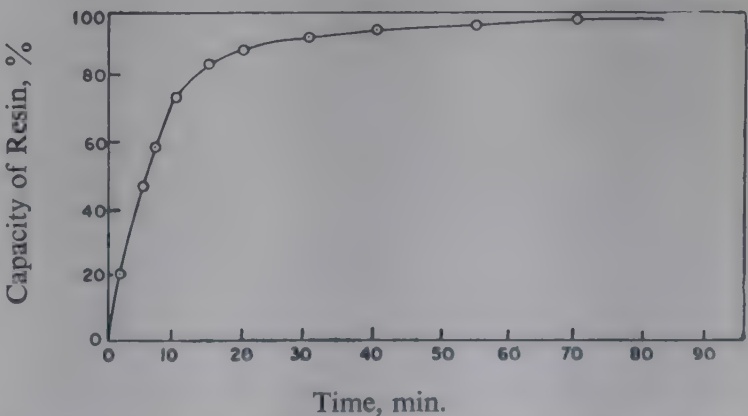


Fig. 1—Plot of Percentage Capacity of Resin with Time Size of Resin —20+ 22 mesh
Molar Concentration 0.1M
Equilibrium $H^+ \rightleftharpoons Na^+$

form of resin. The molecular sorption of electrolyte itself which might be there will not affect the equilibrium constant¹⁵. Thus, the concentration of metallic ion in solution phase at equilibrium was obtained. After knowing the equivalence of exchange at equilibrium, the concentration of metallic ions in resin phase was determined by difference. The equilibrium constant was determined for a particular cation by knowing the concentration of metallic ion in both resin and solution phases. The presumption has been made here that the change in swelling in different forms of exchanger is quite negligible.

All the metal salts were taken in the chloride form except in case of silver salt where it is used in the nitrate form. The results for exchange of uni-univalent and uni-

divalent ions are shown in Tables 2 and 3 respectively.

Experiments have similarly been carried out by taking different particle sizes of resin and also at different temperatures (Tables 4 and 5). Some more experiments have been carried out in a similar manner with a poly-functional cation-exchange resin, Lewatit CNS, in hydrogen-form with other exchanging ions (Table 6).

Results and Discussion

The relative affinities of ions depend on several factors, namely total ion concentration in resin phase, the size of ion concerned, the valancy or the charge of ion, the concentration of external solution and the type of solvent used¹⁶. But if one uses ion of some valency in a particular solvent and exchanges it on a particular

TABLE 2—EQUILIBRIUM CONSTANTS OF UNI-UNIVALENT SERIES

Temperature: $-40 \pm 0.1^\circ\text{C}$
Resin size : $-20 + 22$ mesh (B.S.S.)

Sl. No.	Exchange Equilibrium	Ionic Fraction in Resin Phase, X_R	Ionic Fraction in Solution phase, X_S	Equilibrium Quotient, K_a	Log K_a	Equilibrium Constant, K
1.	$\text{H}^+ \rightleftharpoons \text{Li}^+$	0.8020	0.8904	0.4986	-0.3020	0.497
		0.5351	0.7258	0.4330	-0.3615	
		0.3676	0.5480	0.4794	-0.3193	
		0.2214	0.3680	0.4903	-0.3095	
		0.1108	0.1837	0.5536	-0.2568	
		0.0553	0.0918	0.5791	-0.2372	
2.	$\text{H}^+ \rightleftharpoons \text{Na}^+$	0.7777	0.8944	0.4128	-0.3843	0.566
		0.5420	0.7231	0.4531	-0.3438	
		0.4208	0.5381	0.6233	-0.2053	
		0.2810	0.3571	0.7035	-0.1527	
		0.1570	0.1755	0.8752	-0.0517	
		0.0883	0.0862	1.0270	+0.0116	
3.	$\text{H}^+ \rightleftharpoons \text{NH}_4^+$	0.6706	0.7146	0.8130	-0.0899	1.008
		0.5028	0.5362	0.8744	-0.0583	
		0.3670	0.3536	1.0600	+0.0253	
		0.2142	0.1730	1.2660	0.1025	
		0.1302	0.0835	1.6420	0.2155	
4.	$\text{H}^+ \rightleftharpoons \text{K}^+$	0.6697	0.7075	0.8383	-0.0766	1.035
		0.3784	0.3445	1.1580	+0.0638	
		0.2283	0.1693	1.4510	0.1618	
		0.1191	0.0842	1.4710	0.1675	
5.	$\text{H}^+ \rightleftharpoons \text{Ag}^+$	0.8231	0.6447	2.565	0.4090	4.640
		0.7403	0.4606	3.338	0.5234	
		0.5895	0.2890	3.583	0.5482	
		0.4038	0.1241	4.782	0.6796	
		0.2704	0.0494	7.107	0.8514	

TABLE 3—EQUILIBRIUM CONSTANTS OF UNI-DIVALENT SERIES

Temperature : $40^{\circ} \pm 0.1^{\circ}\text{C}$ Resin Size : $-20 + 22$ mesh (B.S.S)

Sl. No.	Exchange Equilibrium	Ionic Fraction in Resin Phase	Ionic Fraction in Solution Phase	Equilibrium Quotient, K_a	Log K_a	Equilibrium Constant, K
1.	$\text{H}^+ \rightleftharpoons \text{Mg}^{2+}$	0.9130	0.8697	0.3533	-0.4518	1.129
		0.8230	0.6831	0.5791	-0.2372	
		0.7470	0.4942	0.9064	-0.0427	
		0.6293	0.3110	1.0483	+0.0204	
		0.4830	0.1318	1.5495	0.1903	
		0.3189	0.0547	1.6845	0.2265	
2.	$\text{H}^+ \rightleftharpoons \text{CO}^{2+}$	0.9432	0.8630	0.9540	-0.0205	1.694
		0.8663	0.6743	1.1425	+0.0577	
		0.7763	0.4872	1.2563	0.0989	
		0.6864	0.3004	1.7070	0.2322	
		0.4990	1.1276	1.7790	0.2502	
		0.3502	0.0492	2.0875	0.3197	
3.	$\text{H}^+ \rightleftharpoons \text{Mn}^{2+}$	0.9556	0.8490	1.953	0.2906	1.824
		0.8858	0.660	1.785	0.2516	
		0.8023	0.4729	1.810	0.2577	
		0.7200	0.2858	2.460	0.3909	
		0.5347	0.1153	2.514	0.4004	
		0.3090	0.0511	1.710	0.2330	
4.	$\text{H}^+ \rightleftharpoons \text{Ni}^{2+}$	0.8097	0.4961	1.716	0.2245	2.347
		0.7035	0.3097	1.846	0.2662	
		0.6503	0.2164	2.236	0.3547	
		0.5360	0.1312	3.164	0.3353	
		0.4072	0.0477	3.303	0.5189	
5.	$\text{H}^+ \rightleftharpoons \text{Cu}^{2+}$	0.9230	0.8630	0.508	-0.2941	2.932
		0.7821	0.4762	1.424	+0.1535	
		0.6796	0.2920	1.706	0.2319	
		0.5230	0.1186	2.260	0.3541	
		0.4101	0.0378	5.705	0.7563	
		0.2628	0.0106	6.609	0.8201	
6.	$\text{H}^+ \rightleftharpoons \text{Ca}^{2+}$	0.8120	0.4941	1.785	0.2516	3.717
		0.7208	0.3061	2.183	0.3391	
		0.6606	0.2137	2.489	0.3961	
		0.6010	0.1248	3.624	0.5592	
		0.4340	0.0423	4.406	0.6441	
7.	$\text{H}^+ \rightleftharpoons \text{Ba}^{2+}$	0.9610	0.8637	2.039	0.3094	4.025
		0.8980	0.6731	2.056	0.3131	
		0.8390	0.4822	2.700	0.4314	
		0.7455	0.2949	2.911	0.4640	
		0.6131	0.1143	4.262	0.6296	
		0.4335	0.0386	4.853	0.6860	

TABLE 4—EFFECT OF PARTICLE SIZE OF RESIN ON EQUILIBRIUM CONSTANTS

Temperature: $40 \pm 0.1^\circ\text{C}$

Sl. No.	Exchange Equilibrium	Particle size of Resin	Ionic Fraction in Resin Phase, X_R	Ionic Fraction in Solution Phase, X_S	Equilibrium Quotient, K_a	Log K_a	Equilibrium Constant, K
1.	$\text{H}^+ \rightleftharpoons \text{Na}^+$	(-18+20) mesh	0.7830	0.8892	0.4496	-0.3472	0.530
			0.5565	0.7181	0.4933	-0.3075	
			0.4037	0.5381	0.5811	-0.2357	
			0.2503	0.3596	0.5945	-0.2258	
			0.1346	0.1777	0.7198	-0.1428	
			0.0666	0.0888	0.7321	-0.1354	
2.	$\text{H}^+ \rightleftharpoons \text{Na}^+$	(-20+22) mesh	0.7777	0.8944	0.4128	-0.3843	0.566
			0.5420	0.7231	0.4531	-0.3438	
			0.4208	0.5381	0.6233	-0.2055	
			0.2810	0.3571	0.7035	-0.1527	
			0.1570	0.1755	0.8752	-0.0579	
			0.0883	0.0862	1.0270	+0.0116	
3.	$\text{H}^+ \rightleftharpoons \text{Na}^+$	(-30+36) mesh	0.8071	0.8859	0.5391	-0.2683	0.600
			0.5780	0.7196	0.5337	-0.2727	
			0.4224	0.5420	0.6178	-0.2091	
			0.2674	0.3641	0.6376	-0.1955	
			0.1556	0.1792	0.8440	-0.0737	
			0.1020	0.0862	1.2040	-0.0807	
4.	$\text{H}^+ \rightleftharpoons \text{Na}^+$	(-52+60) mesh	0.8421	0.8990	0.6000	-0.2218	0.668
			0.5930	0.7021	0.6187	-0.2085	
			0.4354	0.5500	0.6307	-0.2002	
			0.2723	0.3465	0.7060	-0.1512	
			0.1426	0.1580	0.8862	-0.0520	
5.	$\text{H}^+ \rightleftharpoons \text{K}^+$	(-20+22) mesh	0.6697	0.7075	0.8383	-0.0766	1.035
			0.3784	0.3445	1.1580	+0.0638	
			0.2283	0.1693	1.4510	0.1618	
			0.1191	0.0842	1.4710	0.1675	
6.	$\text{H}^+ \rightleftharpoons \text{K}^+$	(-30+36) mesh	0.8491	0.8742	0.8105	-0.0912	1.128
			0.6380	0.6384	0.9980	-0.0052	
			0.3712	0.3153	1.2820	+0.1080	
			0.2073	0.1480	1.5100	0.1791	
			0.0998	0.0624	1.6650	0.2213	
7.	$\text{H}^+ \rightleftharpoons \text{K}^+$	(-52+60) mesh	0.8583	0.8746	0.8693	-0.0618	1.202
			0.7027	0.7061	0.9834	-0.0072	
			0.3856	0.3121	1.3830	+0.1410	
			0.2015	0.1320	1.6040	+0.2053	
			0.1228	0.774	1.6680	+0.2223	

TABLE 5—EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

(Particle Size: -20+22 mesh (B.S.S.))

Sl. No.	Temperature, °C	Exchange Equilibria	Ionic Fraction in Resin Phase, X_R	Ionic Fraction in Solution Phase, X_S	Equilibrium Quotient, K_a	Log K_a	Equilibrium Constant, K
1.	30	$H^+ \rightleftharpoons Na^+$	0.8286	0.9284	0.3723	-0.4292	0.519
			0.5716	0.7540	0.4350	-0.3615	
			0.4524	0.6283	0.4890	-0.3108	
			0.2692	0.3535	0.6737	-0.1715	
			0.1115	0.1211	0.9106	-0.0407	
2.	40	$H^+ \rightleftharpoons Na^+$	0.7777	0.8944	0.4128	-0.3843	0.566
			0.5420	0.7231	0.4531	-0.3438	
			0.4208	0.5381	0.6233	-0.2055	
			0.2810	0.3511	0.7035	-0.1527	
			0.1570	0.1755	0.8752	-0.0579	
			0.0883	0.862	1.0270	+0.0116	
3.	50	$H^+ \rightleftharpoons Na^+$	0.7927	0.8856	0.4941	-0.3062	0.683
			0.5668	0.7163	0.5193	-0.2845	
			0.4284	0.5155	0.6500	-0.1871	
			0.3051	0.3535	0.8025	-0.0955	
			0.1817	0.1721	1.0670	-0.0283	
			0.0978	0.0849	1.1680	-0.0675	
4.	30	$H^+ \rightleftharpoons Ag^+$	0.8334	0.5568	2.461	0.3910	4.310
			0.7210	0.4771	2.832	0.4521	
			0.5892	0.2777	3.730	0.5716	
			0.3824	0.1104	4.991	0.6982	
			0.2320	0.0417	6.932	0.8408	
5.	40	$H^+ \rightleftharpoons Ag^+$	0.8231	0.6447	2.565	0.4090	4.640
			0.7403	0.4606	3.338	0.5234	
			0.5895	0.2890	3.583	0.5482	
			0.4038	0.1241	4.782	0.6796	
			0.2704	1.0494	7.107	0.8514	
60.	50	$H^+ \rightleftharpoons Ag^+$	0.8320	0.6311	2.896	0.4618	4.842
			0.6792	0.3834	3.405	0.5322	
			0.5810	0.2592	3.965	0.5983	
			0.3815	0.0951	5.867	0.7684	
			0.2486	0.0447	7.406	0.8696	

TABLE 6—COMPARISON OF EXCHANGE EQUILIBRIUM DATA FOR DIFFERENT POLYFUNCTIONAL CATION-EXCHANGE RESINS

(Temperature : $40 \pm 0.1^\circ\text{C}$
(Size of Resins : $-20 + 22$ Mesh (B.S.S.))

Sl. No.	Exchange Equilibrium	SINDEX—C26					LEWATIT—CNS				
		Ionic Fraction in Resin Phase, X_R	Ionic Fraction in Solution Phase, X_S	Equilibrium Quotient, K_a	Log K_a	Equilibrium Constant, K	Ionic Fraction in Resin Phase, X_R	Ionic Fraction in Solution Phase, X_S	Equilibrium quotient, K_a	Log K_a	Equilibrium Constant, K
1.	$\text{H}^+ \rightleftharpoons \text{Na}^+$	0.7777	0.8944	0.4128	-0.3853	0.566	0.8208	0.9020	0.4996	-0.3014	0.741
		0.5420	0.7231	0.4531	-0.3438		0.5932	0.6877	0.6620	-0.1790	
		0.4208	0.5381	0.6233	-0.2053		0.4741	0.5103	1.8650	+0.0260	
		0.2810	0.3571	0.7035	-0.1527		0.1753	0.1668	1.145	0.0587	
		0.1570	0.1755	0.8752	-0.0518		0.0931	0.0823			
		0.0883	0.0862	1.0270	+0.0116						
2.	$\text{H}^+ \rightleftharpoons \text{K}^+$	0.6697	0.7075	0.8383	-0.0766	1.035	0.6527	0.6765	0.8987	-0.0463	1.288
		0.3784	0.3445	1.1580	+0.0638		0.5693	0.4923	1.3620	+0.1344	
		0.2283	0.1693	1.4510	1.1518		0.4588	0.3131	1.861	0.2696	
		0.1191	0.0842	1.4710	0.1675		0.2835	0.1463	2.309	0.3634	
3.	$\text{H}^+ \rightleftharpoons \text{Ag}^+$	0.8231	0.6447	2.565	0.4090	4.640	0.8312	0.5807	3.557	0.5511	5.052
		0.7403	0.4606	3.338	0.5234		0.7121	0.3779	4.076	0.6102	
		0.5895	0.2890	3.583	0.5482		0.5907	0.2395	4.580	0.6608	
		0.4038	0.1241	4.782	0.6796		0.4083	0.1136	5.386	0.7313	
		0.2704	0.0494	7.107	0.8514		0.2709	0.0522	6.750	0.8293	

resin, the affinity changes are due chiefly to change in concentration of external solution. Thus, K_a for exchange reaction, which is a measure of relative affinity of ion, is dependent upon changes in concentration of external solution. The results in Tables 2 and 3 indicate clearly that K_a of ion-exchange reaction is not a constant quantity but varies with equivalent fraction of exchanging ions in resin phase (i.e. X_R). As X_R is dependent upon concentration of external solution (resin weight being constant) K_a varies with concentration of equilibrium solution. The variation of K_a is quite irregular thus it supports the observations of Duncan and Lister¹⁷, Lowen¹⁵, Reichenberg¹⁸ and Bhatnagar⁶. Thus, for any affinity relationship K_a should be referred as constant depending upon particular value of X_R .

Fig. 2 gives the plot for different values of X_R vs X_S for various equilibria. The curves for sodium and lithium exchange with hydrogen form of exchanger have been found to lie below the diagonal (0, 0) (1, 1). It indicates that these exchange equilibria are not favourable and these ions have lower affinity for hydrogen form of resin. Similar results have been obtained by Govindan⁹

in his studies of exchange equilibria of cation-exchange resin from cashew nut shell liquid. In unfavourable equilibria, large quantities of saturating solution will be required to convert the resin completely from one form to the other; so in commercial plants the partial saturation of resin is employed to avoid much loss of regenerants. Except these two curves, all are lying above the diagonal so all the other reactions are favourable.

In Fig. 3 the plot has been made for the logarithms of equilibrium quotient K_a vs ionic fraction of equilibrating ion in resin phase X_R . By applying equation (1), the equilibrium constant K for a certain exchange equilibrium is obtained. In the monovalent series the order of affinity of resin for various cations is lithium < sodium < potassium = ammonium < silver. The selectivity reversal in case of sodium hydrogen exchange in comparison with sulphonated polystyrene-type resins might be due to the presence of weakly acidic groups, such as carboxyl groups, where hydrogen ion readily forms covalent bonds with the carboxyl group⁸.

The values of equilibrium constant for different polyfunctional resins are presented in Table 6 for comparison

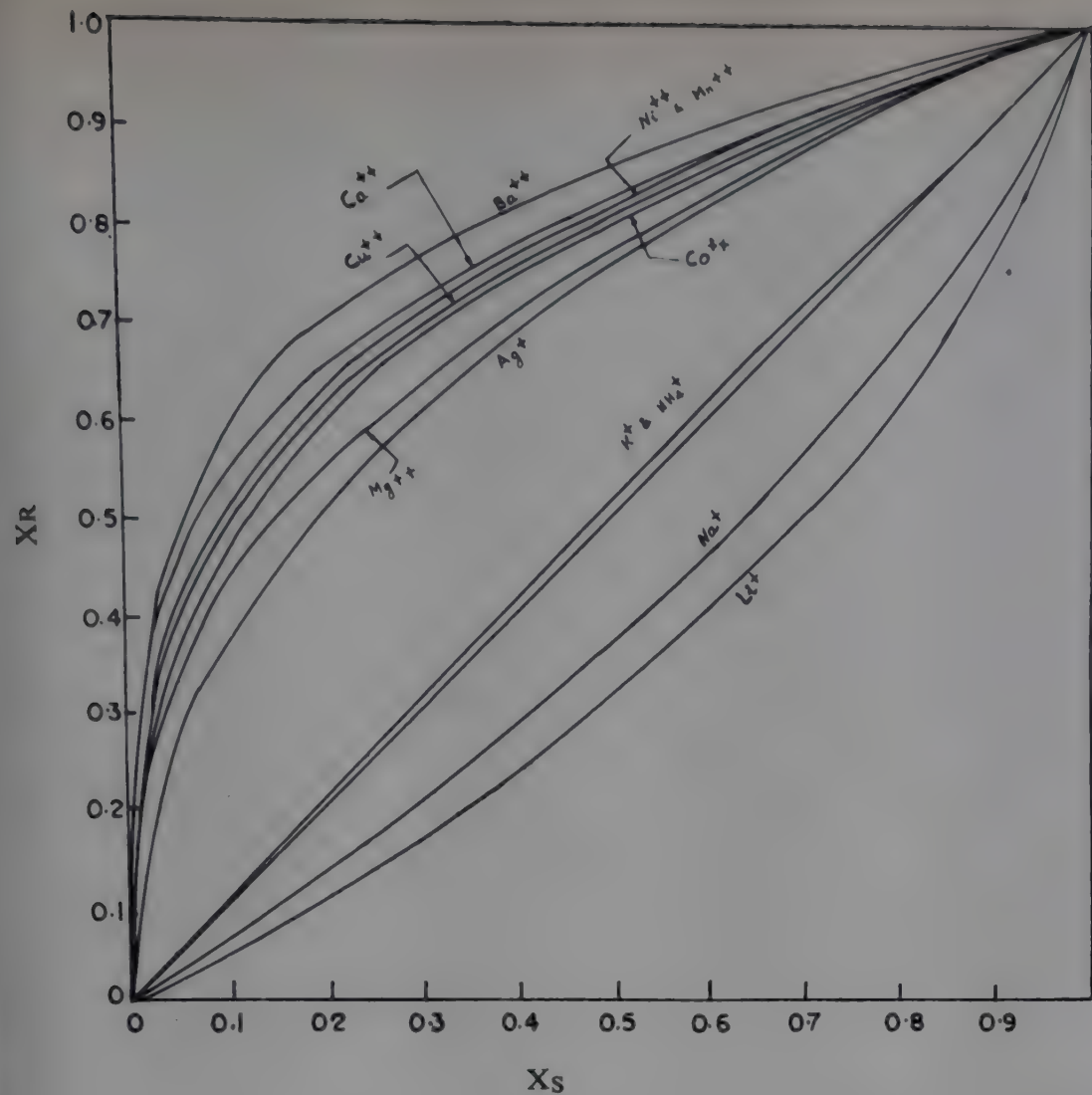
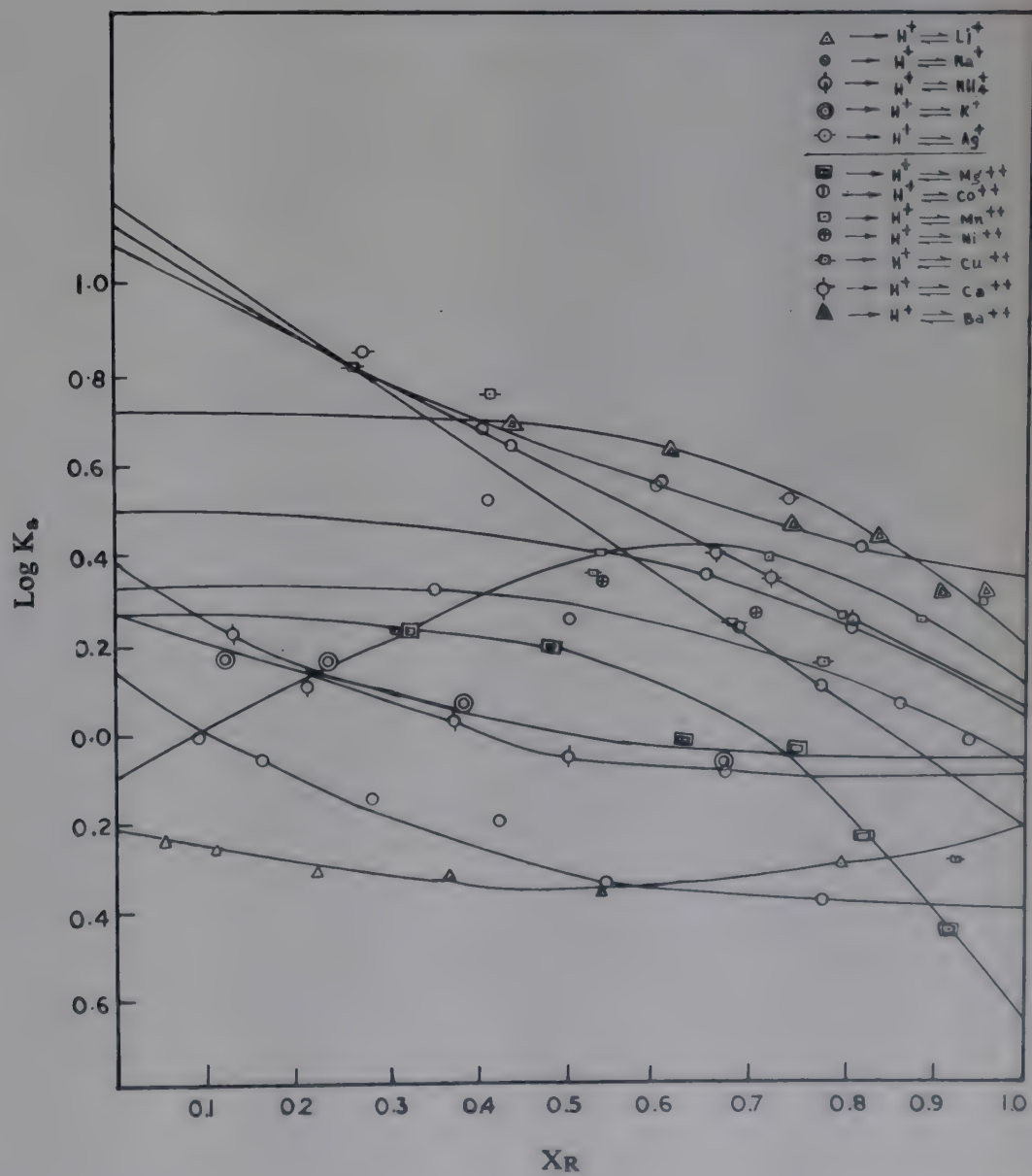


Fig. 2—Plot of X_R against X_S

Fig. 3—Plot of X_R Vs. $\log K_a$



purpose. It can easily be noted from these figures that the behaviour of exchange equilibrium in polyfunctional resins is almost identical.

The data for the equilibrium constants for different divalent ions with hydrogen form of exchanger are presented in Table 3. The exchange equilibria is favoured with all the divalent ions studied here, similar is the case reported with synthetic sulphonic acid resin with all the divalent ions. The affinity for different divalent ions lies in the order: magnesium < manganese < cobalt < nickel < copper < calcium < barium.

The order of affinities for different divalent ions are not related to their atomic number or atomic weights. The selectivity of an ion-exchange resin for divalent ions over monovalent ions varies not only with X_R and X_S but also with C_0 , the total salt concentration of solution, as is seen from equation (3).

Further, in Table 4 the data are being presented for a few exchange equilibria with different particle sizes of resin and in Table 5 the data of exchange equilibria at different temperatures for various ions are given. It is quite conclusive from Table 4 that with the decrease in particle size of resin the value of equilibrium constant increases. It can further be concluded from Table 5 that an increase in equilibrium constant is noted with the increase in temperature.

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A streptomycin-resistant species of bacteria has been noted to occur predominantly on young roots of paddy (78-98 per cent) but with the maturity of the crop, the frequency of this organism started declining and at the time of harvesting only 4-6 per cent of roots yielded the same. As soon as the declining phase of the bacterial species set in, a demateaceous fungus, *Humicola oryzae* appeared and soon became the dominant colonizer (72-80 per cent) of this substrate at harvesting. It has also been demonstrated that the bacterial species concerned is antagonistic towards *Humicola oryzae* and as such the prevalence of the former during the early periods of root-growth is probably the main reason for the absence of the latter during the same period from young paddy roots.

Ecology of Soil Fungi of Rice Fields

III—Antagonistic Microorganisms Occurring on Paddy Roots

By A. C. DAS AND N. K. SHAW,

Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar

In an earlier paper, Das¹ noted that a species of streptomycin-resistant bacteria is always associated with the roots of young rice plants. He also recorded a demateaceous fungus, identified² as *Humicola oryzae*, occurring predominantly on the mature roots of this crop, plated a few weeks before and after harvesting. During further studies, evidences indicating an antagonistic relationship between these two organisms were obtained. Some observations made since then are presented in the present paper.

Materials and Method

Rice of the varieties, Patnai 23 and IR-8 had been grown in the field plots with organic composts and inorganic fertilizers. The roots of the growing crops were collected at least once a month during the whole growing period, cut into small pieces of about 2 cm. long, washed thoroughly in serial changes of sterile water, dried by soaking on sterile filter paper, plated on 1.0 per cent malt agar and incubated at room temperature (23-30°C). The number of root pieces giving rise to the organisms were recorded and expressed as percentage. The streptomycin-resistant bacteria (S.R.B.) and the fungus *Humicola oryzae* were then isolated in pure culture and maintained in 1 per cent malt solution and agar slants respectively.

For studying the phenomenon of antagonism between these organisms, the following methods were used: (a) the roots of paddy IR-8 and Patnai 23 were collected

immediately after harvesting in 1969 and 1968 respectively, and after thorough washings 100 pieces of roots (2 cm. long approx.) were placed on sterilized slides kept in a moist chamber (Petridish with moist filter paper inside) and each was then moistened with 2-3 drops of S.R.B. culture broth grown at least for 10 days in 1 per cent malt solution. Another 100 pieces were moistened with bacterial culture filtrate obtained by centrifuging at 18000 rpm. The control roots were moistened only with sterilized malt solution without bacteria grown in it. Observations were taken under microscope for the presence of *Humicola* after 5 days. (b) Fresh malt agar plates were inoculated by S.R.B. and *Humicola oryzae*, the inoculum being placed at a distance of 2 cm. from each other on the same plate. (c) In another experiment *Humicola oryzae* and S. R.B. were grown on separate malt agar plates and malt solutions respectively. When the fungal colony developed fully, it was flooded by about 20 ml. of 10 days old bacterial culture broth. Control plates were flooded by sterile water. Agar discs of about 5 mm. diam. were then cut out aseptically at intervals from the fungal colonies, washed by gentle shaking in serial changes of sterile water, dried by soaking on sterile filter paper and plated on freshly prepared malt agar plates. In another series, the inoculum discs were similarly treated but washing was avoided. Observations were taken after 7 days.

Results and Discussion

The results on the percentage occurrence of S.R.B. and *Humicola oryzae* on rice roots are given in Tables 1 and 2.

It is seen from the data presented that the bacterial species occurs predominantly from the great majority of root pieces (78-98 per cent) of both the varieties plated in August and September. With the cultivar Patnai 23, this bacterial dominancy persisted through October till 4th November. However, towards the latter part of November the frequency of this organism declined greatly and almost disappeared in December (3-6 per cent). In the case of the cultivar IR-8, this declining phase has started much earlier in the last week of October as this is a crop of a much shorter duration. It is also noted with both the varieties that so long as S.R.B. was dominant on roots, *Humicola* did not appear at all. But as soon as the bacterial frequency showed signs of steady decline, the fungus appeared and soon became the dominant colonizer of the mature but still living roots. Thus, it is evident that the declining of the frequency of S.R.B. coincides with the ripening stage of

paddy crops and this facilitates the colonization of its roots by *Humicola oryzae*.

This microbial succession is possible due probably to the interaction of several factors operating in the field but the antagonism of the bacterial species against *Humicola* is perhaps one of them. It is quite evident from the results (Table 3) that while 63 per cent of control roots have yielded *Humicola oryzae* the moistening of the same with either S.R.B. culture broth or centrifuged filtrate obtained therefrom has inhibited the fungus almost completely. This shows quite clearly that the bacterial species in question is definitely antagonistic towards *Humicola* and an antifungal antibiotic principle elaborated by this bacteria is perhaps responsible for this inhibition. The antagonism was further demonstrated in culture plates. When both the organisms were allowed to grow side by side, they grew well but *Humicola* was noted to grow away from the bacterial colony leaving a zone of about 3-5 mm. of the agar surface uncolonized by the fungus (Fig.1). The streptomycin-resistant bacterial species can, therefore, inhibit the growth of *Humicola* in its vicinity even in agar culture plates. From

TABLE 1—FREQUENCY OF MICROBIAL OCCURRENCE ON ROOTS OF PADDY OF CULTIVAR PATNAI—23, %

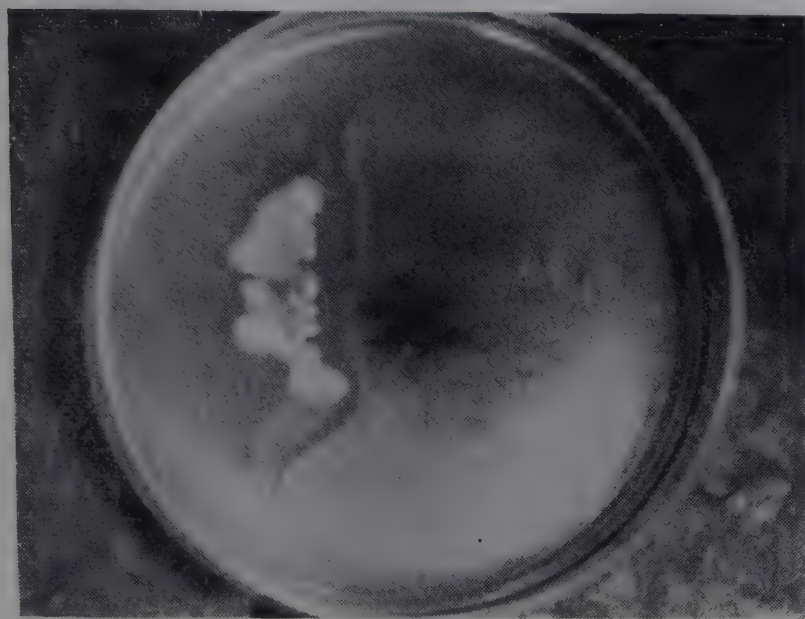
Organisms	30th July 1968	18th Aug.	10th Sept.	9th Oct.	4th Nov.	20th Nov.	4th Dec.	15th Dec.
	Paddy tran. planted						Paddy harvested	
Streptomycin-resistant Bacteria (S.R.B.)	—	78	98	88	75	39	6	3
<i>Humicola oryzae</i>	—	0	0	0	02	42	76	79

TABLE 2—FREQUENCY OF MICROBIAL OCCURRENCE ON ROOTS OF PADDY OF CULTIVAR IR—8, %

Organisms	31st July 1969	21st Aug.	24th Sept.	28th Oct.	6th Nov.	28th Nov.	6th Dec.
	Paddy transplanted					Paddy harvested	
Streptomycin-resistant Bacteria (S.R.B.)	—	91	93	23	6	4	2
<i>Humicola oryzae</i>	—	0	0	68	72	80	78

TABLE 3—ROOTS OF PADDY COLLECTED AFTER HARVESTING, GIVING RISE TO *Humicola oryzae*, %

Treatments	Replications			Mean
1. Roots moistened with S.R.B. Culture broth.	0	2	1	1
2. Roots moistened with S.R.B. Culture filtrate	1	4	0	1.7
3. Roots moistened with malt solution-Control	68	59	62	63.0

Fig. 1—Showing Zone of Inhibition of *Humicola oryzae* Caused by the Bacterial Colony

the results of still another experiment given in Table 4, it can be seen that the flooding of fungal colonies by bacterial culture broth affects the growth potentiality of the fungus markedly. When the inoculum, kept immersed in bacterial broth, was plated without washings heavy

bacterial growth followed from all the discs plated and no fungal growth was noted.

With washed inoculum discs, however, the fungus grew out from the great majority (80-100 per cent) of them even after 48 hours' immersion. No fungal growth, however, was noted from any one of inoculum kept immersed in bacterial broth for 96 hr. This is due to the fact that complete removal of bacteria by washings from the inoculum discs kept immersed for 96 hr. was not obtained; hence bacteria, developing from all the inoculum discs, prevented the fungus from growing out.

Thus, it is evident that if the bacteria and *Humicola oryzae* are brought together and allowed to grow on suitable medium, the former will always inhibit the latter.

Conclusion

The results of experiments described above have shown conclusively that the bacterial species S.R.B. is definitely antagonistic towards *Humicola oryzae* and hence the prevalence of the former on young paddy roots is probably one of the factors for the exclusion of the latter

TABLE 4—PERCENTAGE INOCULUM DISCS GIVING RISE TO *Humicola oryzae*, %

(Fungal colonies immersed)

Period of Immersion, hr.	In Bacterial Culture broth		In Sterile Water	
	Inoculum washed	Inoculum not washed	Inoculum washed	Inoculum not washed
0	100	0	100	100
8	100	0	100	100
24	80	0	100	100
48	80	0	100	100
96	0	0	100	100

from the same substrate. Further research, however, is necessary to work out conclusively whether other factors like secretions from young roots are also playing a part.

Acknowledgement

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Two hybrid annunciator circuits have been designed from indigenously available components, which employ transistors and relays for their switching action. Both the circuits are quite reliable and economical and may be employed in any modern chemical plant.

Hybrid Annunciator Circuits

By G. P. GUPTA,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

In modern chemical industries, specially employing a continuous process, all process variables, e.g. flow, pressure, temperature, level, etc., are controlled by automatic devices. These have the following distinct advantages: (1) minimum cost of production (2) minimum wastage of raw materials, and (3) good quality of the finished products.

If any one of the above process variables crosses the limit of its pre-set value, which is generally termed as abnormality or off-normal condition, it must be indicated to the operator immediately by some means to achieve safety and maximum production. This important job is done by an instrument known as Annunciator, which alerts the operator by the sounding of a horn and lighting a lamp. The following sequence is generally observed during an abnormal condition of a process variable; (i) abnormality is communicated to the annunciator via an electrical contact switch coupled with the process variable; (ii) the horn sounds and the lamp glows which in turn enlightens the operator to the nature of the trouble; (iii) the operator acknowledges

the off-normal condition by pushing the acknowledgement push-button, whereupon the horn is silenced, but the lamp remains lighted; and (iv) when the trouble is rectified, the lamp goes off automatically.

Thus, an annunciator, which is primarily meant for checking abnormalities in a running plant, saves expensive machinery and valuable man-hours and prevents production loss.

Annunciation System

There are mainly three categories of annunciation systems, viz. (i) pneumatic—generally used in refineries in order to prevent explosion (ii) electric or electric-cum-electronic—commonly used in chemical plants and (iii) **solid-state**—may be employed in some new chemical projects.

The second system, employing mainly relays is available indigenously from four firms.* I.T.I. has used quite

*M/s Indian Telephone Industries; Mahindra & Mahindra; Jagriti and English Electric.

complex circuitry which is employed mainly in telephone industry, the second firm has recently brought out in the market an annunciator, employing relays in the de-energized condition and as such may not be preferred by the plant designers. M/s. Jagriti's annunciator though cheapest suffers from the following drawbacks: (i) its high ratings of voltage and current of the trouble contact-points, i.e. about 100 volts and 25 m.a. respectively; (ii) high heat dissipation in the instrument i.e. about 7 watts/channel; (iii) chattering effect of a.c. relays and (iv) it can not be used on d.c. supply. Lastly M/s. English Electric's annunciator which being quite costly, can not handle the large values of contact and lead resistances and also has heat dissipation of about 3 watts/channel.

In this paper a circuit has been described for the annunciator whose material cost is less than the cheapest one and performance and reliability have been found to be better than any one available from the above four firms. The developed circuit is partly transistorized and employ low-voltage d.c. relays.

Annunciator Circuit (Without Flasher)

Two types of annunciators are commonly used—one employing steady-light visual signal and the other flashing light (steady after acknowledging) for the abnormal condition.

The circuit diagram of the two channel non-flasherized annunciator is shown in Fig. 1. If more channels are needed, connections to the points A, B, C & D can be extended further to any number of channels (w.r.t. the common earthing point). The annunciator circuit consists mainly of two parts, viz. the control circuit, which is actuated by the abnormality through the points 1 or 2 w.r.t. the common earthing points and the acknowledge circuit which alerts the attendant by sounding the horn. The circuit described here accepts only the close contact abnormalities, which is generally preferred but if the converse is desired the circuit can be modified slightly.

The control circuit consists of two transistors, T_1 and T_2 , one biasing resistance R_1 , one surge absorber-capacitor C_2 and one low voltage operated d.c. relay, RLC. Normally all the relays are kept in the energizing

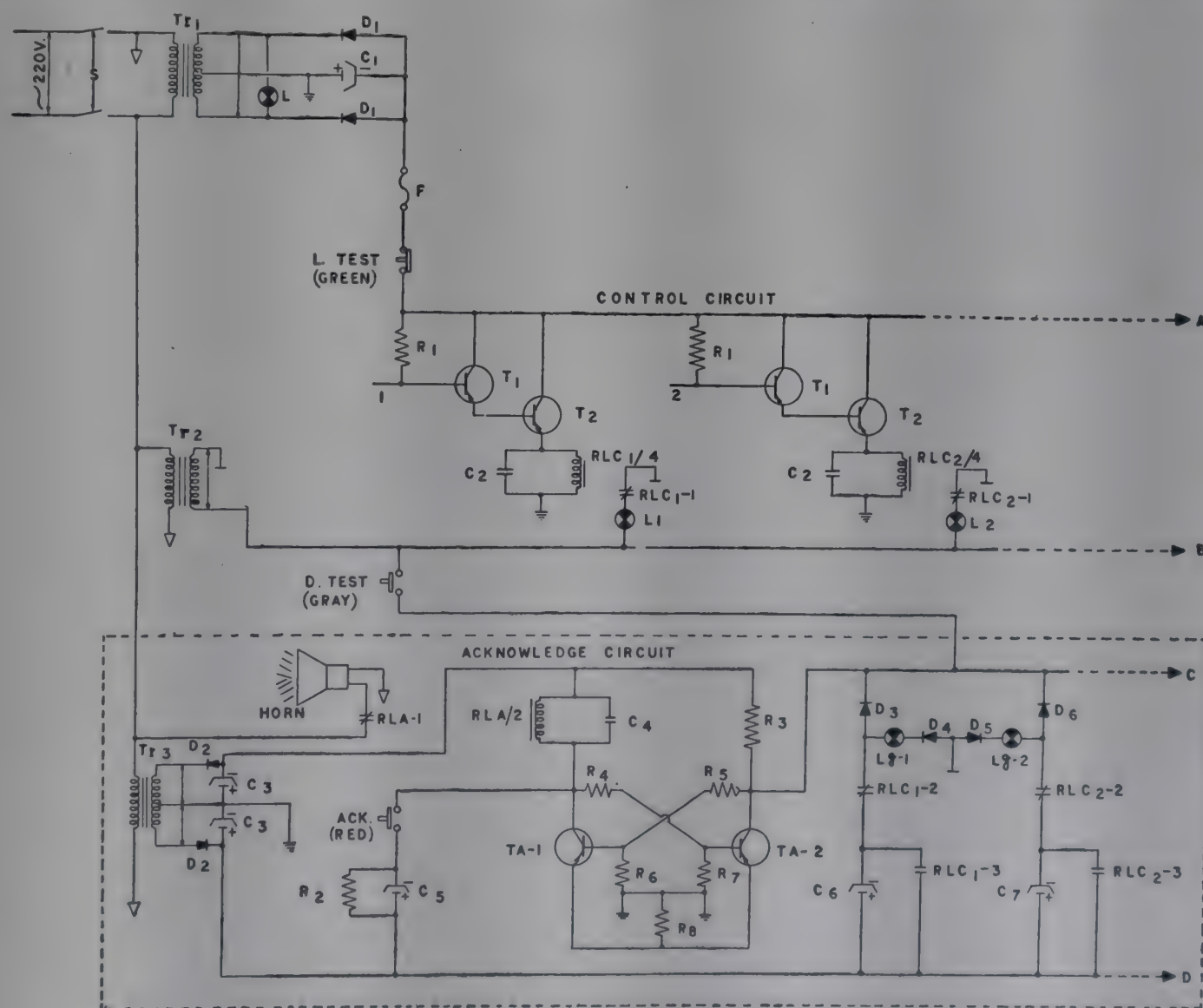


Fig. 1—Annunciator Circuit without Flasher

[Note: All Contact Points of Relays are in Synchronization with De-energized State of Relays.]

state. If an abnormality is communicated by any one of the channels by short-circuiting the trouble point to the ground which makes the relay of that channel to de-energize/, say, for example the abnormality comes to point 1 which puts the relay RLC_1 off, making RLC_2-1 close, lighting the lamp L_1 of a name plate and simultaneously RLC_1-3 opens and RLC_1-2 closes which in turn momentarily reverse biases T_{A1} through R_5 and R_6 , making the flip-flop to change its state i.e. the relay RLA is de-energized in turn making the contact $RLA-1$ close, sounding the horn. Thus, the control circuit has passed the abnormal signal to the operator by sounding the horn and lighting the lamp L_1 with the help of acknowledge circuit. The operator acknowledges the abnormality by pushing the acknowledgement push-button (Red) which in turn momentarily reverse biases T_{A2} through R_4 and R_7 compelling the flip-flop to change its state again i.e. the relay RLA is energized, horn silences and the acknowledge circuit is ready to accept any new abnormality from any one of the remaining channels. If the trouble shown by the enlightening plate is rectified, lamp L_1 turns off automatically and the control circuit one is also now ready to accept any new abnormality.

A flip-flop arrangement is utilized for the acknowledge circuit, in which the relay, RLA is normally kept in the energizing state i.e. T_{A1} is fully conducting and T_{A2} is cut off in turn the collector of the later is approximately at the negative supply potential. Whenever any abnormality comes through the relay contacts, the transistor T_{A1} is cut off, in turn de-energizing the relay, RLA . Same way it is changed to its initial state by pushing the acknowledgement push-button. R_2 is used to discharge the capacitor C_5 and makes it ready for any new acknowledging. For similar reasons relay points RLC_1-3 and RLC_2-3 are used across the capacitors C_6 and C_7 respectively. The diodes D_3 and D_6 are used to check the charging of a capacitor by any other charged capacitor when a new abnormality comes over some existing abnormalities in different channels. i.e. the capacitor C_6 and C_7 must be charged through R_3 only and discharge through the respective relay points. Thus, each acknowledging channel is in a position of accepting an abnormality independently, whether the other channels are under abnormal or normal conditions.

The plants' safety and minimum production-loss are the main criteria for utilizing the annunciator. It is quite harmful to the plants' safety if the annunciator is unable to alert the operator about an abnormality due to its component failure. 'L—Test' push-button is provided

for testing the lamps as well as the horn. If it is depressed, supply to the RLC relays is cut off which make them de-energize, in turn all the lamps glow and horn sounds, indicating that the whole circuit is functioning well. Any type of defect in the control circuit or failure of its d.c. supply will de-energize the RLC relay, result of an audio and visual signal. If the d.c. supply of the acknowledge circuit fails, the relay RLA will de-energize result in sounding the horn.

The push button 'D-Test' is provided for testing the diodes D_3 and D_6 . This test is necessary because failure (open circuit) of D_3 or D_6 will make that channel totally ineffective which is quite dangerous to the plants' safety. As push button 'D-Test' is pushed further the green lamps L_{g1} and L_{g2} , housed in the respective compartments of L_1 and L_2 must glow uniformly, non illuminating compartment will indicate the failure of any one of the series diodes i.e. open circuit of D_3 or D_4 in channel one and D_5 or D_6 in channel two and over-illumination indicate the short circuiting of any one of the series diodes of the respective channels. Over-illumination will result only if L_{g1} and L_{g2} are of proper voltage and current ratings to suit the forward resistance values of the series diodes. Short circuiting of any one of the series diode reduces the total resistance of that channel which makes the lamp of the channel to glow brightly. D_4 and D_5 are used only to avoid the interference among the channels. This 'D—Test' does not affect the functioning of the acknowledge-circuit by any means.

Flasherized Annunciator Circuit

This type of circuit is favoured by many plant designers. It has the advantage over non-flasherized type that any new abnormality is accompanied by a flashing visual signal (timely no/off, and being steady after acknowledging) and so in a very broad panel it is easily detectable over the existing steady abnormality signals. It has only disadvantage that the lamp life is reduced due to flashing.

The circuit diagram of a two channel flasherized-annunciator is shown in Fig. 2, which has the same control circuits as in Fig. 1. The circuit can be extended to any number of channels by further connecting more channels to the points A, B, C, D, E and F. If the point G is shorted to the points H and I (Fig. 2), the circuit behaves as non-flasherized annunciator.

The flasher circuit used for flashing the lamps is a single transistor R-C oscillator based on charging and discharging of the capacitor C_6 through R_4 (also R_{in} of T_F) and R_3 respectively.

The acknowledge circuit consists of all d.c. relays which are normally kept in the energized condition. The

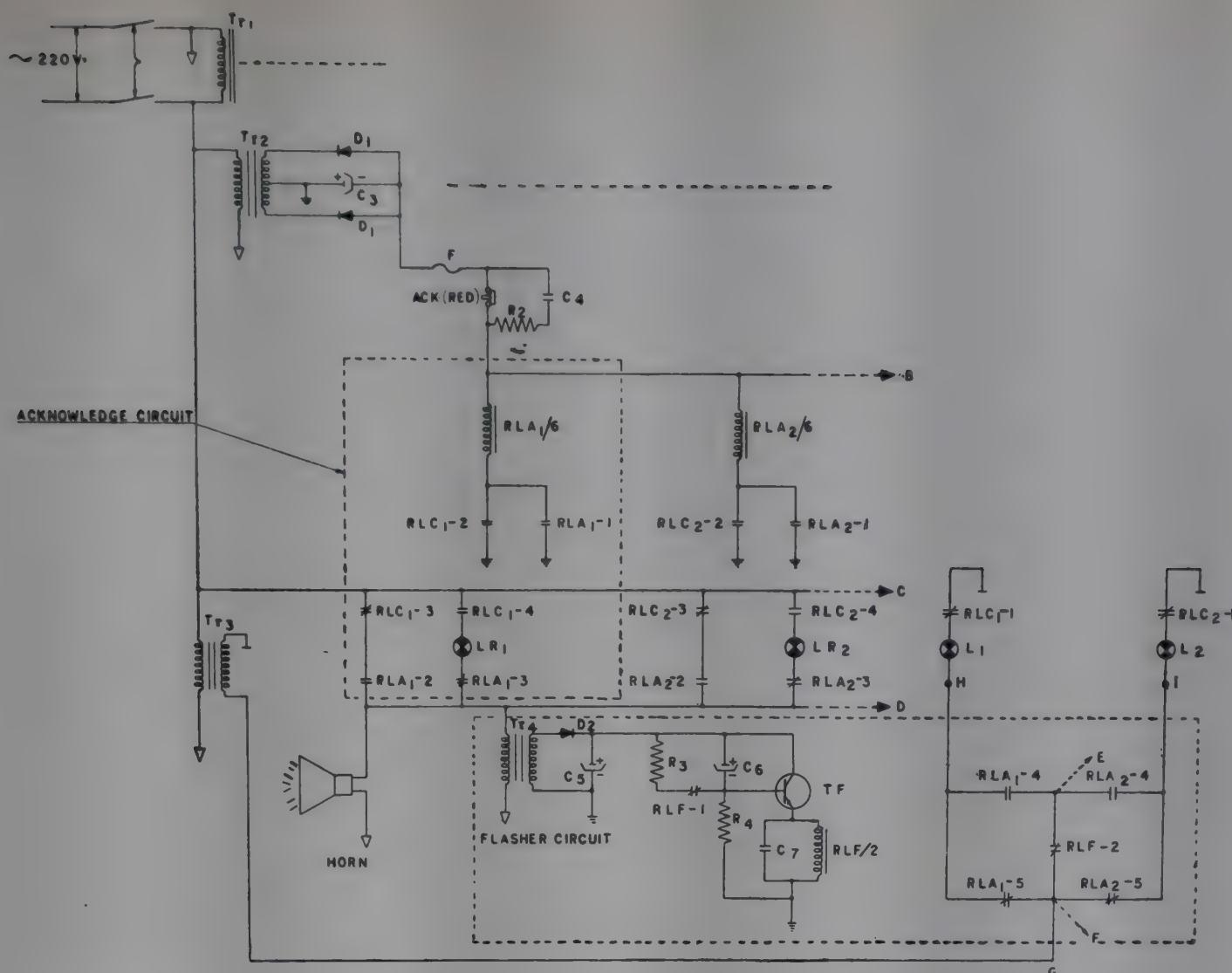


Fig. 2—Flasherized Annunciator Circuit

relay points RLC_1-2 and RLC_2-2 are closed due to the energizing state of RLC relays, whereupon RLA relays are also energized i.e. in the normal condition both types of the relays, RLC and RLA, are energized. Now RLC_2-3 is open and RLA_1-2 close, i.e. there is no power to the horn through this relay-point-channel. Similar is the case for the other channel containing the relay points RLC_2-3 and RLA_2-2 ; hence the horn is silent. The channel containing the red lamp LR_1 is also open as because RLC_1-4 is close but RLA_1-3 open and similar is the case for the channel containing the red lamp LR_2 . So there is no power in the horn through these two channels also. Hence, in the normal condition the horn is silent and lamps are off.

If E and D represent the energizing and de-energizing state of relays then the normal condition of the annunciator circuit may be denoted by EE, where first latter signifies the state of RLC relay while second that of RLA relay. The function of the complete circuit is as follows:

Assuming that the abnormality comes to point 1 of the control circuit, the state of relay-pair will be $D_1 E_1$, making the horn to sound. Same time flasher also

gets the power through the same relay points, RLC_1-3 and RLA_1-2 ; the relay point $RLF-2$ is alternately making and breaking the lamp supply to flash the lamp L_1 . Till the time of acknowledging, RLA_1 is energized, keeping RLA_1-4 close and RLA_1-5 open. After acknowledging, the state of relay pair becomes $D_1 D_1$, flashing stops, lamp steady and horn is silenced. This state will be there till the abnormality at point 1 is existing. If the trouble is rectified the state of the relay-pair becomes $E_1 E_1$, making the lamp L_1 off. Once the acknowledging is done, the lamp is steady irrespective of the arrival of any new abnormalities at any other points because the lamp L_1 gets the power directly from the point RLA_1-5 .

The sequence of the state of any relay-pair during an abnormal condition, can be summarized as E E, D E, D D and E E. The same sequence is followed if d.c. supply of the control circuit is cut off or any defect occurs in that circuit. The relay points RLC_1-4 and RLA_1-3 in series of the red lamp LR_1 and RLC_2-4 and RLA_2-3 in series of LR_2 are used to give the audio and visual signal if d.c. supply of the acknowledge circuit fails or any acknowledging relay goes out of order.

The failure of the acknowledge circuit is governed by the state ED which is quite different from the abnormality sequence and does not disturb it by any means.

The transistor-circuits included in the annunciator are fully tested for their successful performance between 0 to 50°C and does not compel to be employed in the airconditioned control rooms.

With these arrangements, it is understood that the circuit is quite reliable and assures the full safety of the plant.

Special Features

The circuits have the following redeeming features: (1) Indigenous components are utilized in both the circuits. (2) The first circuit is quite economical because only one relay per channel is used along with a common master relay instead of two relays per channel, as normally is the case. The second is economical in the sense that its performance and reliability are better compared to others, with the approximate same component values. (3) Maximum open circuit voltage across the trouble contact point is only 15 volts and current through the contact 0.5 m.a., which reduces the possibility of forming the contact resistance across it. (4) It can handle lead and contact resistances upto the value of 8 k. ohms, which is a quite large value compared to the existing

annunciators and is ideal for telemetry. (5) Heat dissipation of the first circuit in its normal condition is about 0.8 watt. and that of the other 1.5 watt per channel, which is a quite low value compare to the other circuits. (6) If a 12 volts d.c. operated horn is employed instead of 230 volts A.C. then the whole circuit can be made to run from 12 volts storage batteries, in case of power failure. (7) The maintenance is quite easy; testing and repairing can be done in 'ON' condition of the instrument, without affecting the other channels if a 12 or 24 volts operated horn is employed.

Acknowledgements

The author is grateful to Sri J. Banerjee for the valuable discussions and to Sarbasri J. Satyanason and Sri I. K. Suri, Chief and Dy. Chief Engineers (Instrumentation) respectively, P and D Division, for their kind co-operation and encouragement in the completion of the work. Thanks are also due to Sarbasri Gopal Krishnan and S. K. Randev for some helpful discussions with them.

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A number of pure zinc oxide samples have been analysed spectrographically using d.c. arc for the impurities present in them. Lead, iron, copper, silver, manganese, magnesium, aluminium, silicon, bismuth and cadmium have been simultaneously determined by diluting the sample with graphite in the ratio of 3:2 with cobalt as internal standard.

Spectrographic Estimation of Impurities In Pure Zinc Oxide

By R. C. P. SINHA, K. C. SINGHAL AND B. K. BANERJEE,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Zinc oxide is widely used in paints, pharmaceuticals and rubber industry. It has important uses in chemical industry, in the production of various types of catalysts used for, formic acid decomposition, dehydrogenation of isopropanol, conversion of carbon mono-oxide, methanol synthesis, etc. The zinc oxide used in the manufacture of catalysts should be of high purity as the impurities may adversely affect the efficiency of the products. Therefore, it is necessary to determine the impurities in the zinc oxide batch before its selection for use.

Most of the impurities in zinc oxide samples used for the present investigation are very low and so it is difficult to determine them by usual chemical method. Spitzer¹ estimated some elements in zinc oxide by atomic absorption spectrometry. In our samples a number of elements escaped detection in the normal working solutions by this technique. Instead of concentrating the impurities, spectrographic method has been used for simultaneous determination of impurities, viz. lead, iron, copper, silver, manganese, magnesium, aluminium, silicon, bismuth and cadmium, in the samples. Moreover, by simply scanning the plate, taken for quantitative analysis, additional impurities (if present) can also be detected.

Zinc oxide burns smoothly in d.c. arc and sometimes it is deliberately added to the sample for smoothening the arc. Since in our case, zinc oxide is the base itself, no necessity was felt to use any buffer. When samples were

arced as much, it was found that the iron and silicon lines were fainter than those observed when the samples were diluted with graphite powder. A sample to graphite ratio of 3:2 was used. Cobalt has been used as internal standard² as it was absent in the samples.

Experimental

Sample and Standard Preparation: Six typical zinc oxide samples were taken up for the present analysis. All the samples were oven dried and mixed with graphite powder, containing 0.6 per cent of specpure cobalt powder, in the ratio of 3:2.

For the preparation of synthetic standard No. 1 (Table 1) suitable weighed quantities of specpure or G.R. quality salts—mostly oxides—of the elements to be determined were mixed with a specpure zinc oxide base. Subsequent standards were made by progressive dilution with zinc oxide. To each of the synthetic standards graphite powder (with 0.6 per cent cobalt) was mixed in 3:2 ratio.

Instrument and Procedure: KCA-1 quartz spectrograph (Russian), Hilger non-recording microphotometer and d.c. power supply unit (Indian make) were used. National ultrapurity 1/4" diam. graphite rods were used for electrodes. The lower electrode was having a 45° conical crater whereas the upper electrode was made with conical end. Illford N-30 plates (9×24 cm.) were used.

TABLE 1—CONCENTRATION OF ELEMENTS IN SYNTHETIC STANDARDS, PPM

Standard Number	Pb	Fe	Cu	Ag	Mn	Al	Si	Bi	Cd
I	2,000	1,000	40.0	10.0	20.0	40.0	2,000	10.0	100
II	1,000	500	20.0	5.0	10.0	20.0	1,000	5.0	50
III	500	250	10.0	2.5	5.0	10.0	500	2.5	25
IV	250	125	5.0	1.25	2.5	5.0	250	1.25	12.5
V	125	62.5	2.5	0.62	1.25	2.5	125	0.62	6.2
VI	25	12.5	0.5	0.12	0.25	0.5	25	0.12	1.2

About 75 mg. of the samples and synthetic standards were packed in the crater of the electrodes and were arced at 10 amp. An exposure of 45 sec. was given for the spectral range of 2550 to 3500 Å keeping a slit width of 12 μ . After processing the plate, microphotometric measurements were made on suitable analytical line pairs (Table 2). The simple log deflection ratio method was used for drawing the working curves as the plate was quite clear and background was absent near most of the line pairs. In case of silver line (3382.962 Å), the clear plate deflection was adjusted on the background itself which was quite low. The values were calculated from the working curves and are given in Table 3.

TABLE 2—SELECTED ANALYTICAL LINE PAIRS

Sl. No.	Element	Wave Length, Å	Internal Standard Å
1.	Pb	2833.069	Co 2987.162
2.	Fe	3020.640	Co 3013.596
3.	Cu	3273.962	Co 3260.819
4.	Ag	3382.891	Co 3385.224
5.	Mn	2794.817	Co 2987.162
6.	Mg	2795.530	Co 2987.162
7.	Al	3092.713	Co 3089.595
8.	Si	2881.578	Co 2987.162
9.	Bi	3067.716	—
10.	Cd	3261.057	—

Results and Discussions

Out of the impurities detected in the zinc oxide samples bismuth (present in samples 3 & 5) and cadmium

TABLE 3—IMPURITIES IN ZINC OXIDE SAMPLES, PPM

Sample Number	Pb	Fe	Cu	Ag	Mn	Mg	Al	Si	Bi	Cd
1.	44.7	13.5	0.32	0.59	0.62	45.7	6.2	269.2	—	tr
2.	10.5	4.6	0.23	0.17	—	10.7	2.4	28.8	—	—
3.	1,259.0	5.4	0.91	—	10.96	8.3	5.4	134.9	tr	tr
4.	11.3	16.6	1.10	0.71	—	11.1	3.8	138.0	—	—
5.	785.2	7.4	1.82	—	1.02	8.0	4.1	66.1	tr	tr
6.	16.2	5.4	0.63	0.23	0.83	15.8	2.5	79.4	—	—

— not detected.

tr traces

(present in samples 1, 3 & 5) could not be estimated as their lines were very faint for density measurements and as such they have been given as traces (Table 3). It is found that silver is absent in samples 3 and 5 and manganese is absent in 2 and 4, whereas other impurities are present in all the samples though in varying quantities. Lead was found quite high in samples 3 and 5.

Though the internal standard method was used, equal quantities of samples and standards were packed in the electrodes to get more accurate results. A sample-to-graphite ratio of 3:2 was found suitable for enhancing the line intensity of many elements which are suppressed

in pure zinc oxide matrix. The present method is simple, sensitive and accurate enough for our purpose in the selection of the material.

Acknowledgement

The authors are thankful to Dr. S. K. Ghosh, Assistant Superintendent (PRW), for his valuable suggestions.

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- (Original mss. received on Jan. 7, 1970)

The crystallographic properties of choline dipicrylamine has been studied by means of x-ray diffraction of the single crystal. The rotation and the Weissenberg photographs showed that the crystal belongs to the monoclinic system having cell dimensions: $a=10.45 \text{ \AA}$, $b=10.21 \text{ \AA}$, $c=22.25 \text{ \AA}$ and $\beta=84^\circ$. The probable space group is

$P \frac{2}{m} (C_{2h}^1)$

X-Ray Study of Choline Dipicrylamine

By M. L. KUNDU, J. N. KAPOOR AND S. K. GHOSH,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

This laboratory has been investigating on the possibilities of obtaining organic compounds by replacing the metallic ions from dipicrylamine chelates. Thus, choline dipicrylamine, $C_{17}H_{18}N_8O_{13}$, mol. wt. 542.35 and m.p. between 200° and 210°C was prepared from magnesium dipicrylamine and choline chloride (Kapoor, J. N. and Sarkar, J. M. unpublished work). The present investigation comprises determination of crystallographic properties of choline dipicrylamine, by x-ray diffraction from single crystals as well as from powder.

Well-developed single crystals of choline dipicrylamine were grown from its saturated solution in acetone under controlled evaporation. The crystals obtained were deep red in colour and shaped as elongated pris-

matic blades. The size of a typical crystal was $3 \text{ mm.} \times 1 \text{ mm.} \times 0.5 \text{ mm.}$

The preliminary optical study, carried out with an optical microscope, showed the crystal to be perfect biaxial with moderate optic axial angle and negative in character. One set of cleavages was running parallel to the elongation of the crystal, and the extinction angle with respect to the cleavage traces was 14° . Strong inclined dispersion viewed under microscope showed the monoclinic character of the crystal.

The axial lengths were determined from rotation photographs about the proposed (100)-, (010)- and (001)- axes. The zero-level and the first layer line normal beam Weissenberg photographs about these axes were

also taken in a Stoe Integrating Weissenberg camera of dia m. 57.3 mm. using $\text{CuK}\alpha$ radiations. The angles between the reciprocal axes a^* , b^* and c^* , measured from the zero level Weissenberg photographs, were $\alpha^*=90^\circ$, $\beta^*=96^\circ$ and $\gamma=90^\circ$

The axial angles were calculated from these values using the standard formulae¹ while the lengths from the d-values measured from the Weissenberg photographs were found to be consistent with those obtained from rotation photographs. The values are:

From rotation photographs:	From Weissenberg photographs:
$a = 10.45\text{\AA}$	$a = 10.45\text{\AA}$
$b = 10.21\text{\AA}$	$b = 10.22\text{\AA}$
$c = 22.25\text{\AA}$	$c = 22.28\text{\AA}$
$\alpha = 90^\circ$, $\beta = 84^\circ$ and $\gamma = 90^\circ$	

From these values, it was confirmed that the crystal belongs to the monoclinic system.

The volume of the unit cell was determined to be $2361\text{\AA}^3$. The density of the crystal was measured by the flotation method using a mixture of bromoform and xylene. The measured density 1.582 g.cm.^{-3} indicated the number of molecules per unit cell (Z) to be four. The theoretical density, calculated from the x-ray measurement on the assumption that $Z=4$, is 1.525 g.cm.^{-3} .

From the indices of the reflections on the Weissenberg photographs, no systematic absences of reflections were found, showing the crystal to be of the primitive class and screw axes and glide planes are absent. So, only the symmetry 2, m, or $2/m$ is possible. Since there are four molecules per unit cell, the two molecules should be related to the other two by a centre of symmetry. The presence of a centre of symmetry in the unit cell could be confirmed by Wilson's method² and that described by Howells, Phillips and Rogers³. The probable space group is, therefore, $P\frac{2}{m}(C_{2h}^1)$.

The powder photograph of the sample was taken in a Guinier camera using $\text{CuK}\alpha$ radiations. The d-values with relative intensities measured from this photograph are shown in the next column.

Acknowledgements

The authors wish to express their thanks to Dr. B. K. Banerjee for his keen interest in this work. Thanks are also due to Sri J. M. Sarkar for suggesting the problem and to Sri R. Chowdhury for providing optical data.

No. of Lines	d in $\text{\AA}$	Rel. Intensity	No. of Lines	d in $\text{\AA}$	Rel. Intensity
1	10.9	vvw	41	3.00	vw(Br)
2	10.2	vw	42	2.95	vvw
3	9.7	ms	43	2.925	vvw
4	9.2	s (Br)	44	2.855	vvw
5	8.8	m	45	2.800	s(Br)
6	7.3	vvw	46	2.752	m
7	6.3	vw	47	2.730	w
8	5.95	vw	48	2.630	vvw
9	5.85	vvw	49	2.590	vvw
10	5.62	vw	50	2.530	vvw
11	5.45	m	51	2.500	vvw
12	5.25	vvw	52	2.470	vvw
13	5.07	ms	53	2.420	vvw
14	5.00	s	54	2.370	vvw
15	4.90	vvw	55	2.350	vvw
16	4.82	vw	56	2.330	vvw
17	4.57	vw	57	2.300	vvw
18	4.52	ms	58	2.270	vvw
19	4.45	vw	59	2.240	vvw
20	4.33	w	60	2.220	vvw
21	4.20	m	61	2.190	vvw
22	4.15	ms	62	2.170	vvw
23	4.00	vvw	63	2.120	vw
24	3.92	m	64	2.090	vw
25	3.89	vvw	65	2.050	vvw
26	3.75	vvw	66	2.030	vw(Br)
27	3.70	w(Br)	67	2.000	vvw
28	3.66	w	68	1.875	vvw
29	3.59	vs	69	1.859	vvw
30	3.55	vs	70	1.842	vvw
31	3.50	vvw	71	1.825	vvw
32	3.47	m(Br)	72	1.795	vvw
33	3.43	vvw	73	1.780	vvw
34	3.40	vw	74	1.745	vvw
35	3.33	vw	75	1.685	vvw
36	3.30	m(Br)	76	1.580	vvw
37	3.22	vvw	77	1.570	vvw
38	3.18	vw	78	1.550	vvw
39	3.12	vvw	79	1.450	vvw
40	3.09	w			

Further work is in progress.

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Estimation of Nitrate in a Mixture of Nitrite and Nitrate by X-ray Method

By AJIT ROY AND S. K. GHOSH,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

In the manufacture of sodium nitrite, sodium nitrate has been found to be associated with sodium nitrite during the crystallization. Hence, for purity and quality control sodium nitrate content is required to be determined during the crystallization process.

The usual chemical methods for determining nitrate in a mixture of nitrite and nitrate are time-consuming and less accurate. Information on the crystalline form and state of aggregation can not be obtained by these methods. In view of this, an attempt has been made to develop a method for the estimation of nitrate in a mixture of sodium nitrite and sodium nitrate by x-ray method.

Description of the Method

The quantitative analysis by x-ray diffraction method is based upon the fact that intensity of the diffraction line, characteristic of the substance under consideration, depends on the concentration of the substance in the mixture. The intensity of the diffraction line can be measured from its peak height or area (integrated intensity)

The analysis can be done directly or by using an internal standard. The former has several advantages over the internal standard technique and this has been discussed in an earlier paper¹.

Experimental

Materials: Reagent grades of sodium nitrite and sodium nitrate were used as reference compounds. The impurities were checked by taking their diffraction pat-

terns. Six different well crystallized sodium nitrite samples collected from the sodium nitrite pilot plant* were used for the present investigation. The materials were finely ground, dried and stored in a desiccator.

Counting Procedure: Philips X-ray diffractometer PW 1050/51 with Geiger counter was used for the quantitative analysis. Filtered $\text{CuK}\alpha$ radiation with nickel filter was used. A strip chart was run at a scanning speed $1^\circ/\text{min.}$ with 2 sec. time constant in order to check for interference and to select the locations for background measurements. The intensities of the lines were determined from Geiger counts by setting the Geiger tube position manually at the desired angle. The operating conditions for the diffractometer were as follows: X-ray tube 40 KV, 20 mA, detector Geiger-Muller counter tube, 1650 V; multiplication 1; scale factor 64; time constant 2 sec.; scatter slit 1° , scanning speed $1^\circ/\text{min.}$ and paper speed 200 m/hr.

The intensity of the $2.311\text{\AA}2\theta$ ($2\theta=38.4$) for sodium nitrate maximum was used as the reference line for intensity measurements. Since there was no overlapping of lines due to nitrite in the desired angular region, the integrated intensity measurements were directly made from the counts. The counts were corrected for the corresponding background value.

Calibration Curve: Five samples containing sodium nitrate and sodium nitrite in the proportions 2:98, 5:95, 10:90, 15:85 and 25:75 respectively were prepared on weight per cent basis under identical conditions. A calibration curve was drawn by plotting peak heights against the known mixture of nitrate and nitrite as

* of P & D Division at Sindri.

prepared above. The calibration curve is shown in Fig. 1.

Analysis of Nitrite Samples: The samples of nitrite were grounded in an agate mortar and the intensity measurements were made from the counts at the desired angle of sodium nitrate. By referring to the calibration curve (Fig. 1) the intensities of each sample of sodium

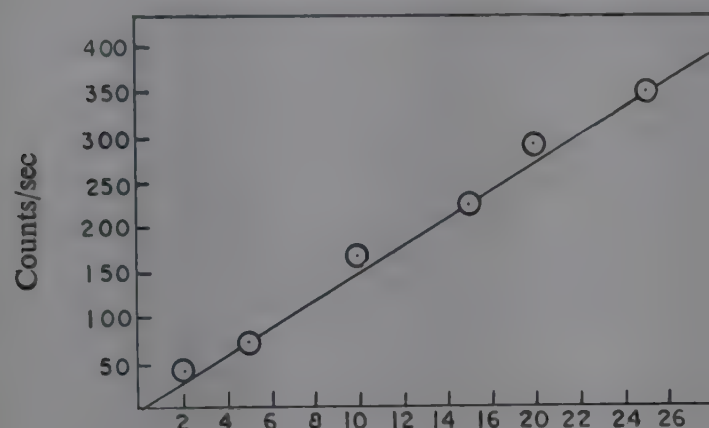


Fig. 1—Mixture of Nitrate and Nitrite (%)

nitrite were used to determine the percentages of sodium nitrate in them.

Results

The results are shown in Table 1.

It can be seen from Table 1 that nitrate content determined by X-ray method compares favourably with that obtained by chemical analysis and thus provides a reasonably accurate method for quick estimation of nitrate in a

TABLE 1—INTENSITY MEASUREMENTS AND ESTIMATION OF SODIUM NITRATE IN SODIUM NITRATE

Samples	No. of Counts/ sec. (corrected)	Sodium Nitrate from Fig. 1, %	Sodium Nitrate Determined by Chemical Ana- lysis, %
A	60	4	3.6
B	130	9.2	8.5
C	190	13.2	12.9
D	48	3.4	3
E	40	2.8	2.3

(All values have been corrected for background)

nitrate-nitrite mixture. Further, it furnishes a direct evaluation of different phases other than nitrite and nitrate present in a matrix.

Acknowledgements

The authors wish to express their thanks to Sri Chinmoy Sen, Dy. Chief Engineer (PD), for suggesting the problem, and to Dr. B. K. Banerjee, Additional Supdt. (PRW), for his keen interest in this work.

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The effectiveness of water and dilute nitric acid (0.01N) on the leaching of chloride ions from the fibrous glass insulating materials has been studied with reference to their textural changes caused by corrosion on their surface. It has been observed that the chloride ion extracted by both water and dilute nitric acid increases with increasing leaching period upto 12 hr. Practically no more chloride ion is liberated on further leaching beyond this period. Again, neither of the leachants has any marked corrosion effect on the surface of the glass fibres. But the quantity of chloride ions extractable in dilute nitric acid is always higher than that in water when compared under similar leaching conditions. This is because of the fact that unlike water dilute nitric acid is capable of extracting chloride ion which are absorbed on the surface of the glass fibres without breaking their network structure. These chloride ions are likely to be released easily from fibrous glass insulating materials in actual plant conditions and enhance stress corrosion cracking of stainless steel equipments. Extraction procedure in dilute nitric acid may, therefore, be adopted as a standard for the determination of the soluble chloride in those materials when intended for insulating the stainless steel plant equipments.

Leaching Characteristics of Chloride From Fibrous Glass Insulations

By H. ACHARYYA, A. K. SAMSUDDIN AND H. ROY,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

Presence of soluble chloride in insulating materials is not desirable as it causes stress-corrosion cracking of stainless steel vessels and pipes when applied for insulation purposes. The tolerable limit which causes such corrosion is still not known with certainty but it is believed that insulating materials having more than 35 ppm soluble chloride may have serious detrimental effect on stainless steel equipments¹.

It is known that anions may be adsorbed on the glass surface; this is because a glass surface is in a pronounced state of non-equilibrium and its disordered asymmetrical structure is the source for all solid state surface reactions, like epitactic inter-growths and adsorption phenomena². Water-soluble chloride salt may be present as impurities in the glass wool insulations. A part of their chloride ions may similarly be adsorbed on the surfaces of the glass fibres from the solution of their salt either during manufacture or moisture absorption at the later stage. Usually leaching with water can not remove the adsorbed ions completely from surfaces of solid particles. The exchangeability of fluorine ions in glass surfaces has been studied by Specht³. He concluded that fluorine ions are not strongly fixed on the glass structure. It is, therefore, likely that the adsorbed chloride ions may be

released easily from the surfaces of glass fibres when used in the plant for insulation purpose where the conditions are much more drastic than water extraction alone. The adsorbed chloride ions should, therefore, be considered as a part of total soluble chloride of the glass wool samples.

There are several standardized procedures for the estimation of chloride in solution⁴. But the method for the determination of soluble chloride in fibrous glass insulating materials has not yet been standardized. It is worth while to mention here that before standardizing such a method, the leaching characteristics of chloride ions from fibrous glass materials using different leaching agents must be known. But the effectiveness of different reagents for leaching out these chloride ions from such materials has not so far been studied in detail.

Again, breakdown of network structure of glass fibre is also possible during leaching. Chlorine ions, which may also be present in the network structure, are more firmly held than the surface⁵. These ions are likely to be leached out as a result of a breakdown. For the extraction of the soluble chloride, care should, therefore, be taken to select such a leachant which is effective only for extracting the adsorbed chloride ions along with other soluble chlorides that may exist as separate phases along

with glass fibres and at the same time it does not materially corrode their surfaces. Considering this, an attempt has been made in the present investigation to study the leaching characteristics of chloride from fibrous glass insulating materials with different leaching agents and to examine the alteration of surface texture so caused due to corrosion by the leachants.

Experimental

Two fresh glass wool samples of different fibre diameter (designated as I & II having diameter 25 and 40 micron respectively) were taken for this investigation.

Leaching of Chlorides: About 5-6 g. of glass wool fibres (weighed accurately) were taken in a 500 ml. beaker. 100 ml. of distilled water or 0.01N nitric acid (chloride-free) was then poured to the sample. The beaker was covered with a watch glass and placed on a hot plate. The content of the beaker was allowed to boil slowly for different time intervals, viz. 2, 6, 12 and 18 hr. The liquid level was adjusted from time to time to make up any loss due to evaporation by distilled water or 0.01N nitric acid as the case may be. After boiling, the supernatant liquid was filtered and the solid residue washed with the same liquid twice or thrice. The volume of the filtrate was finally made up in volumetric flask. Chloride was determined in 10 ml. aliquot of the clear filtrate by the Mohr method⁴, (titration was carried out by a micro-burette). In this method the pH of the extract was adjusted to 7-10 using sulphuric acid or sodium hydroxide (both chloride-free). To 10 ml. of the filtrate, a few drops of potassium chromate indicator solution was added and titrated with standard silver nitrate solution to a pink yellow end-point. The blank titration with water and nitric acid was also performed in each case. The chloride content so extracted vs. time of each sample is shown in Fig. 1.

Surface Examination of the Leached Glass Fibres: The corrosion of the glass fibres caused by the leachants was examined under moderate magnification in almost similar way, as dimming test performed for the chemical durability of glass⁶.

The surfaces of the fibre samples after leaching with water and 0.01N nitric acid for 18 hr. were examined by a polarized microscope using transmitted plane polarized light and magnification 400x. The untreated fibres were also examined similarly. The microphotographs are shown in Fig. 2.

Results and Discussion

It is evident from Fig. 1 that chloride extracted by

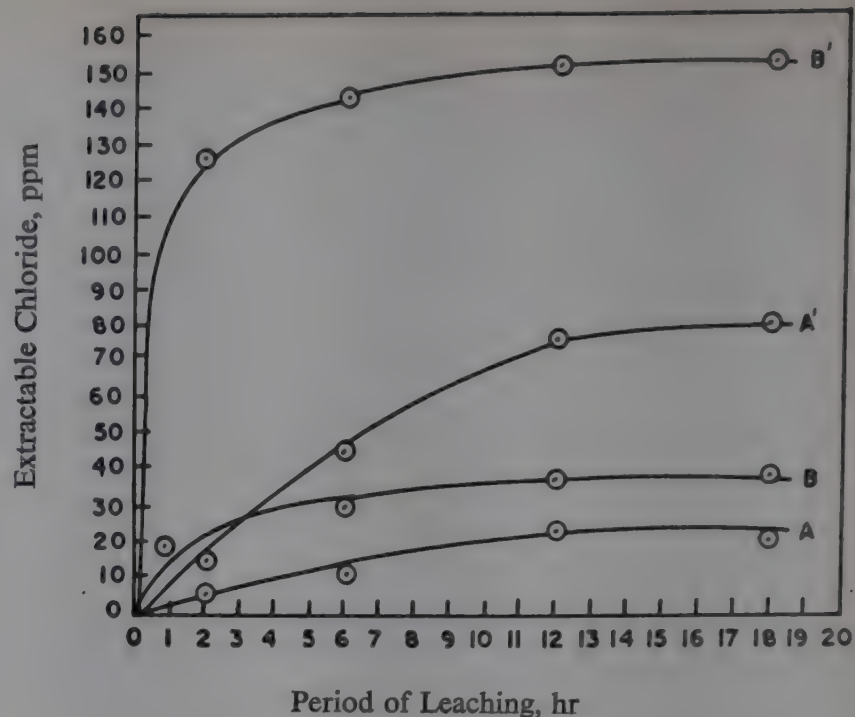


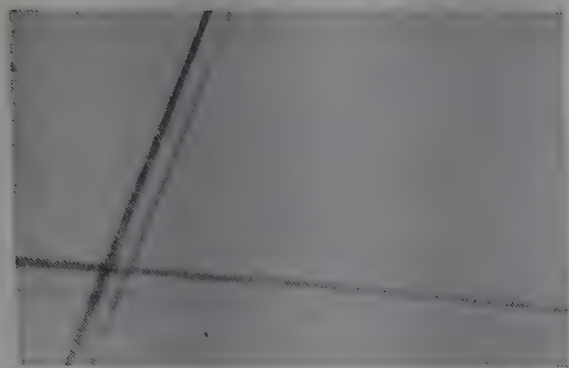
Fig. 1—Extractable Chloride from Fibrous Glass Insulating Materials using Different Leaching Agents

A, A' leached in water; B, B' leached in 0.01N nitric acid.
A, B and A'B' represent samples I & II respectively.

both water and dilute nitric acid from the glass fibres increases with increasing leaching time upto a period of 12 hr. Practically there is no more increase of this value on further leaching. But the chloride leached out by water is much less than that by dilute nitric acid. Thus, in a water medium only 22 and 76 ppm of chloride are leached out from samples I and II after 12 hr. of leaching, whereas those leached out in nitric acid medium after similar period of leaching are 37 and 152 ppm respectively.

In order to see whether there is any corroding action on the surfaces of glass fibres by the leaching agents, particularly by dilute nitric acid, the surfaces of the leached glass fibres were compared with those of untreated ones. It is evident from the microphotographs (Fig. 2) that there is no marked corrosion effect (with respect to any fogging, pitting or roughening) in water as well as in nitric acid medium even after 18 hr. of leaching. This indicates that the network structure inside the glass fibres is not affected by dilute nitric acid. In this connection, it is interesting to mention here that Yoshiki⁷ demonstrated that glass fibres of $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ composition are very resistant to acids and alkalis. It is, thus, evident that dilute nitric acid is effective for extracting the absorbed chloride ions without breaking the net-work structure of glass fibre. Usually, water-insoluble chlorides are not present as a separate phase in the glass wool insulating materials. Extraction procedure with dilute nitric acid may, there-

Sample I



A



B

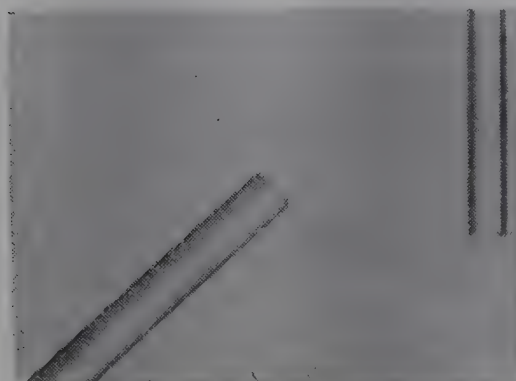


C

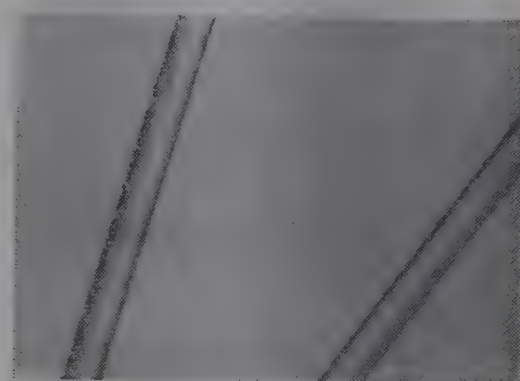
Sample II



A



B



C

Fig. 2—Microphotographs of Fresh and Leached Fibre Glass Samples (Plane polarized light, magnification 400×)
A, B & C represent fresh, water and 0.01N nitric acid leached (18 hr.) samples

fore, be adopted as a standard for determination of soluble chloride in those materials.

Acknowledgement

Thanks are due to Dr. B. K. Banerjee, Additional Supdt., for his keen interest in this investigation.

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(Original mss. received on Feb. 26, 1970)

Effects of ammonium sulphate and other ammonium, sodium and potassium salts on the viscosity of calcium carbonate slurry have been studied. Reduction in apparent viscosity of the slurry has been observed by the addition of these salts. The effectiveness of the salts in reducing the viscosity is in the order ammonium sulphate > ammonium chloride > sodium sulphate > potassium sulphate > ammonium nitrate > potassium chloride > potassium nitrate > sodium chloride > disodium phosphate.

Effect of Some Ammonium and Alkali Metal Salts on the Viscosity of Calcium Carbonate Slurry

By RAJENDRA SINGH AND A. K. ROY,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

In a previous communication,¹ results were given of the study on the effect of sodium polyphosphates on the viscosity of slurries of chalk obtained as a by-product during the manufacture of ammonium sulphate from gypsum by the Merseburg process. The effects of some ammonium and alkali metal salts on the viscosity of slurries of calcium carbonate—both chemically pure and the by-product samples—have been further studied; the results of which are reported in this paper.

The by-product chalk sample collected from the secondary filters of ammonium sulphate plant in Sindri was dried at 60°C and ground to pass through a 100 mesh (B.S.) sieve and the slurries were prepared from the—100 mesh sample. Analysis of this chalk sample is given in Table 1.—200 mesh B.D.H.-make calcium carbonate was also used in the present study.

The viscosity measurements were made by a Brookfield synchroelectric viscometer model LVT-E in a cylindrical pyrex glass vessel of 5 cm. diam. All the measurements were made at 30 rpm with spindle no. 2. The different salts were added to the slurry in the form of solid, and after each addition the stirring was continued until the lowest value was attained. The salts used were all of B.D.H. (A.R.) quality.

The results given in Tables 2 and 3 show that the apparent viscosities of the slurries of by-product chalk

TABLE 1—CHEMICAL ANALYSIS OF THE BY-PRODUCT
CHALK SAMPLE

Ingredients	% by wt.
SiO ₂ +Insoluble	15.12
R ₂ O ₃	2.22
CaO	43.88
MgO	0.49
SO ₃	3.72
Nitrogen as N	0.23
Loss on ignition	34.33

and pure calcium carbonate progressively decrease with the addition of increasing amounts of ammonium sulphate. The introduction of gypsum or a form of stable calcium sulphate, prepared by repeated heating of gypsum, also shows some reduction in the viscosity of calcium carbonate slurry (Table 3); the reduction by the anhydrous calcium sulphate sample is comparatively less.

TABLE 2—EFFECT OF AMMONIUM SULPHATE ON THE VISCOSITY OF THE BY-PRODUCT CHALK AND CALCIUM CARBONATE (B.D.H.) SLURRIES

(NH ₄) ₂ SO ₄ , g/100g. Slurry	Viscosity of By-product Chalk at 35°C, cp.		(NH ₄) ₂ SO ₄ , g./ 100g. Slurry	Viscosity of CaCO ₃ (B.D.H.) at 35°C, cp		
	60% w/w Slurry	65% w/w Slurry		15% w/w Slurry	20% w/w Slurry	25% w/w Slurry
0	220	850	0	200	400	950
2	205	690	1	160	250	700
4	185	665	2	130	220	450
6	165	625	3	100	190	400
8	125	520	4	90	150	350
12	115	430	6	80	110	260
16	105	350	8	70	100	230
24	95	250	10	60	95	200
32	—	200	12	55	90	180
			16	—	—	150
			20	—	—	130
			24	—	—	110

TABLE 3—EFFECT OF GYPSUM AND ANHYDROUS CALCIUM SULPHATE ON CALCIUM CARBONATE (B.D.H.) SLURRY

CaSO ₄ .2H ₂ O, g./100g. of Slurry	Viscosity of 20% Slurry at 35°C, cp.	CaSO ₄ , g./100g. Slurry	Viscosity of 20% Slurry at 35°C, cp.
0	400	0	400
0.1	320	0.1	370
0.2	290	0.2	340
0.3	280	0.3	340
0.5	270	0.5	350
0.7	270	0.7	350
1.0	275	1.0	365

TABLE 4—EFFECT OF SOME SALTS ON THE VISCOSITY OF CALCIUM CARBONATE (B.D.H.) SLURRIES

Salt, g/100g. Slurry	Viscosity of 20% w/w Slurry at 35°C, cp.							
	NH ₄ Cl	NH ₄ NO ₃	KCl	K ₂ SO ₄	KNO ₃	NaCl	Na ₂ SO ₄	Na ₂ HPO ₄
0	400	400	400	400	400	400	400	400
1	370	340	350	330	370	390	300	350
2	350	305	330	290	350	360	250	350
3	300	290	320	280	310	340	240	330
4	290	270	305	260	290	315	220	310
6	270	250	275	220	250	290	190	230
8	250	220	225	220	230	260	150	200
10	210	200	205	—	215	240	140	180
12	160	180	185	—	185	220	130	160
14	125	160	165	—	—	—	120	155
16	105	145	150	—	160	190	110	150
20	75	110	120	—	140	170	90	—

Other ammonium, sodium and potassium salts studied have also acted as viscosity depressants (Table 4). Ammonium salts are more effective than the corresponding sodium and potassium salts. Greater reduction was observed with sulphates than with the corresponding other salts. The effectiveness of the salts is in the order ammonium sulphate > ammonium chloride > sodium

sulphate > potassium sulphate > ammonium nitrate
potassium chloride > potassium nitrate > sodium
chloride > disodium phosphate.

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(Original mss. received on March 20, 1970)

In one of the units of FCI Ltd., some stainless steel vessels in the air-separation and nitrogen wash units of an ammonia plant were found damaged by corrosion at several places during installation and commissioning. Carbide precipitation coupled with corrosive environment, especially chloride from the insulating materials, might be the main factors responsible for the failure of the stainless steel vessels.

Corrosion of Cold Box Equipment in an Ammonia Plant—a Case History

By K. M. VERMA, S. C. VERMA, M. P. GUPTA,
H. GHOSH, B. R. CHAKRAVORTY AND A. K. ROY,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

In one of the units of FCI Ltd. some stainless steel vessels in the air-separation and nitrogen wash units of an ammonia plant were observed to be damaged by corrosion at several places during installation and commissioning and in all 25 such vessels were observed to be damaged. A detailed examination revealed two types of corrosive attack, viz. (1) general pitting distributed at random in most of the vessels but sometimes concentrated in localized areas with or without the deposit of a brown rust, (2) leaks that have subsequently developed after commissioning of the plant on or very close to the weld seams. There was no definite correlation between the points of leakage and the pitted or rusted spots; leaks even occurred at places where no pits or rusting had been observed. In some cases, it had been observed that even after the leaks had been patched up by welding, fresh ones started at nearby positions.

All the equipment in the cold boxes were packed by pearlite and slag wool insulating materials. During operation, the conditions are completely non-corrosive on the outside as well inside of the vessels, the temperature being subzero and the environment being an inert one devoid of oxygen. For investigation, samples were taken from the following two portions: (1) bottom cover of nitrogen liquefier (air separation unit); (2) top cover of carbon monoxide wash column (nitrogen wash unit). The samples did not contain any leaks.

During fabrication of the dished end portions, the bottom cover of nitrogen liquefier had been cold-formed while that of top cover of carbon monoxide wash column

was hot-formed. To investigate into the causes of corrosion, chemical analysis and metallographic examination were carried out with the samples cut out from the above two portions. The chloride content of the insulating materials was also analysed.

Test and Observations

A. NITROGEN LIQUEFIER (BOTTOM COVER)

Chemical Analysis: The samples on analysis gave the following results: chromium 16.8 per cent and nickel 9.1 per cent.

Metallographic Examination: For metallographic examination samples were cut out from following portions: (i) weld with parent metal; (ii) knuckle region (supposed to be under maximum stress); and (iii) portion away from the weld and knuckle regions.

(i) Weld with parent metal (Fig. 1)—The structure of the weld metal is dendritic while the parent metal is austenitic. The grains of the austenite show up with a dotted appearance indicating the precipitation of carbide all along the austenitic grain boundaries. There is extensive carbide precipitation along the dendrite in the weld metal as well.

(ii) Knuckle region (Fig. 2)—The structure is austenitic with presence of slip bands and fine carbide precipitation all along the austenitic grain boundaries.

(iii) Portion away from the weld and knuckle region (Fig. 3)—The structure is austenitic. The grains of the austenite show up with a dotted appearance indicating fine carbide precipitation all along the grain boundaries.

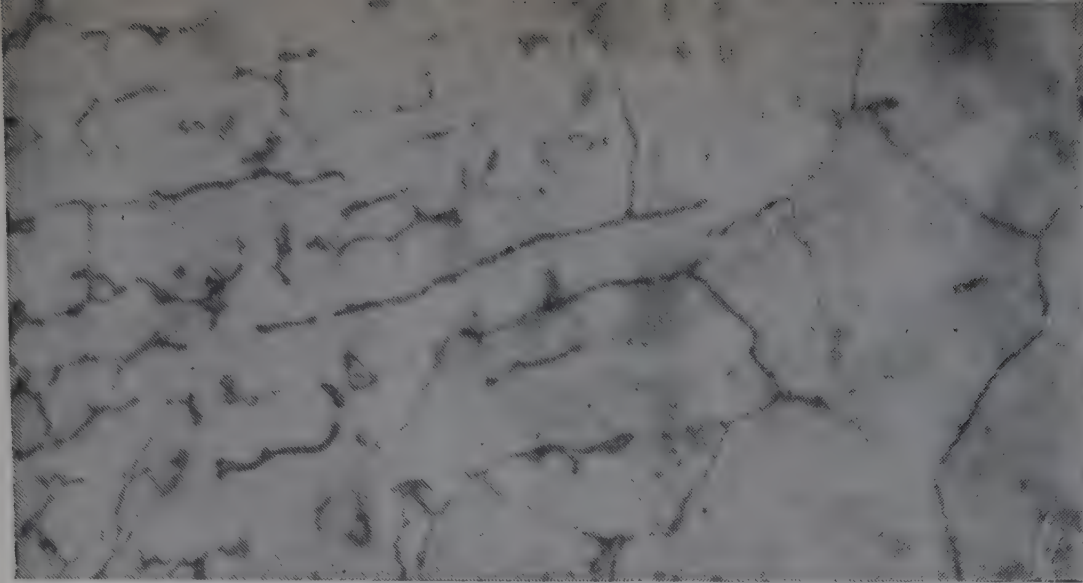


Fig. 1—Photomicrograph of a transverse section across the junction of weld and parent metal showing the dendritic structure of the weld metal while the grain boundaries of the austenite show up with a dotted appearance due to the precipitation of carbide. X (450)

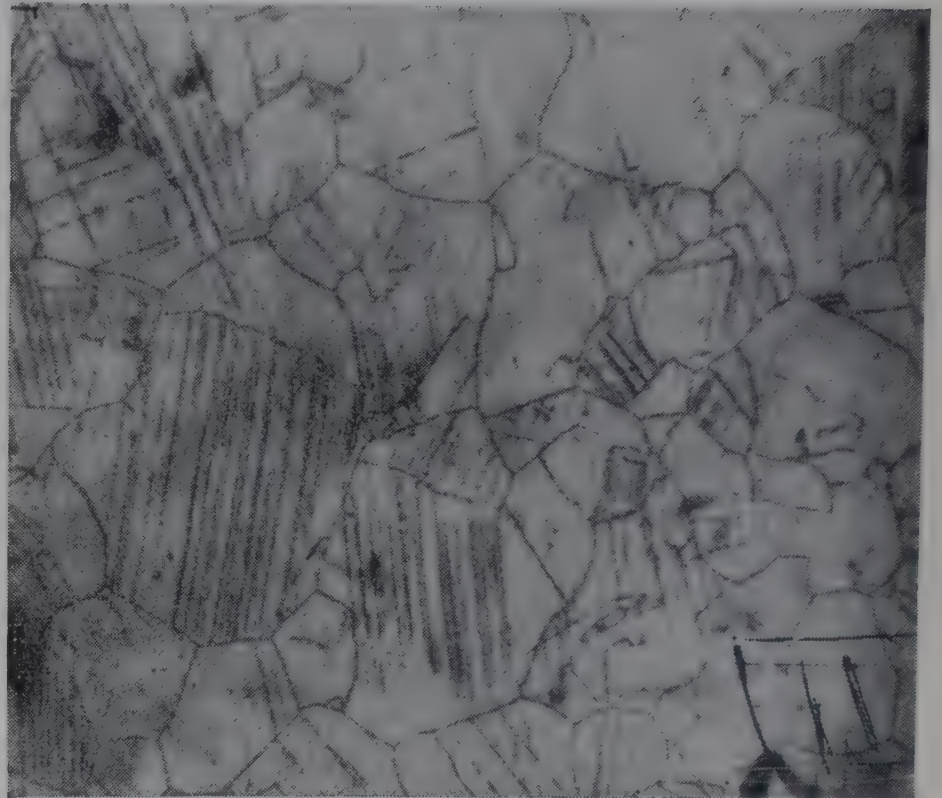


Fig. 2—Photomicrograph of the outer surface of the knuckle region showing austenitic grains with presence of slip bands and fine carbide precipitation all along the grain boundaries and slip planes. X (450)

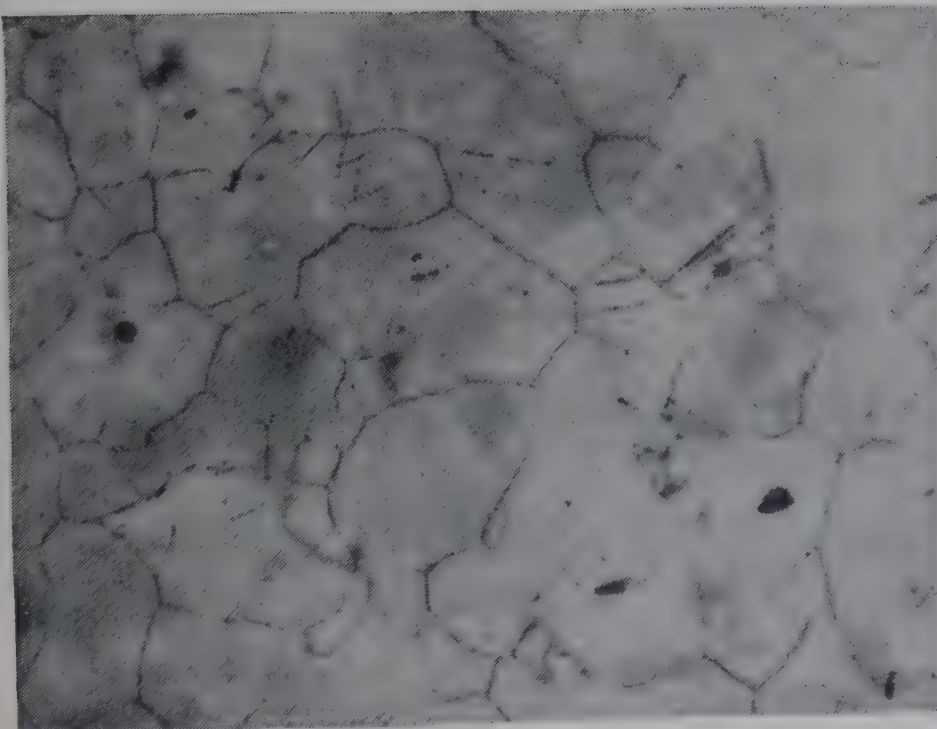


Fig. 3—Photomicrograph of a transverse section showing the grain boundaries of the austenite with a dotted appearance due to the precipitation of carbide X (450)

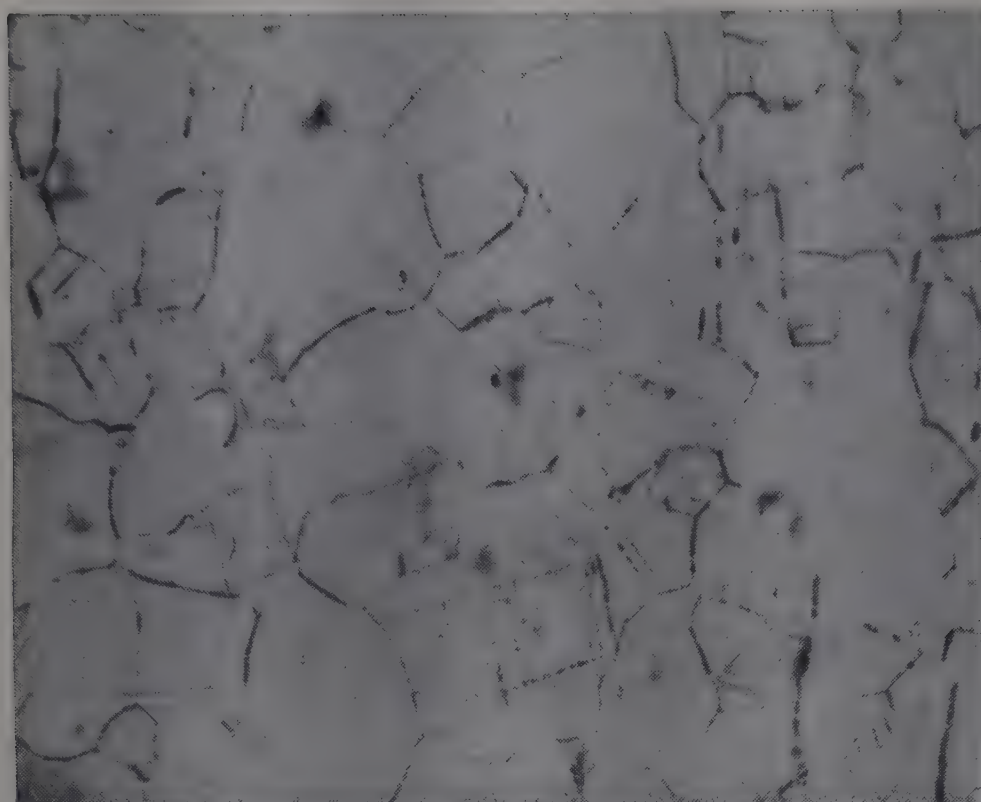


Fig. 4—Photomicrograph of a transverse section showing austenitic grains and carbide precipitation at the grain boundaries
X (340)

B. CARBON MONOXIDE WASH COLUMN (TOP COVER)

Chemical Analysis: The samples gave the following results: Chromium 17.8 per cent and nickel 9.2 per cent.

Metallographic Structure: The portions away from the welded seam were taken for study. Fig. 4 shows a transverse section. The structure is austenitic with carbide precipitation along the grain boundaries. The pattern of carbide precipitation is quite different from that of the nitrogen liquefier bottom cover. It is in form of discontinuous bands at the grain boundaries.

Chemical Analysis of the Insulating Materials: The insulating materials gave the following characteristics:

Material	Chloride Content as Cl, ppm
Pearlite	238.5
Slag wool	341.3
Black globules present in the slag wool	2829.5

Discussion

The chemical analysis of the stainless steel shows the material to be type AISI 304 and this is according to the specification. The metallographic structure of the parent metal shows the structure to be austenitic with intense carbide precipitation, the pattern of which is continuous all along the grain boundaries in the nitrogen liquefier while it is discontinuous in the form of bands in the carbon monoxide wash column. This difference is due to the fact that the dished end of carbon monoxide wash column has been hot-formed and that of nitrogen liquefier cold-

formed. The analysis of the insulating material shows contamination with appreciable quantities of chloride, particularly the black globules in the slag wool contain a very high percentage of chloride.

With the precipitation of carbide in the stainless steel chromium impoverished grain boundaries are very much susceptible to corrosion. In some cases, even process or rain water has been reported to cause corrosion under such conditions. In the present case, the conditions might have been aggravated by the presence of appreciable quantities of chloride in the insulating material which are liable to affect the vessels because of moisture pick-up during storage. The effect was likely to be more aggressive at the stressed portions, viz. at or near the welded seams and places where working has been done as stresses increase the rate of development of crack. The high concentration of chloride in the globules of the slag wool might have been more detrimental.

It has also been reported that if the steel is susceptible to intercrystalline corrosion, pitting corrosion becomes intercrystalline and it penetrates the metal along the grain boundaries. This may explain the leakages in some of the pitted vessels. The outside rusting and pitting might have also been caused to a small extent by the possible contact of sea water during transportation.

In summarizing the above findings, it can be said that carbide precipitation coupled with corrosive environment especially chloride from the insulating material might be the main contributing factors to the failure of stainless steel vessels.

(Original mss. received on Feb. 18, 1970)

From economic considerations the dimensions of a bag should be minimum; at the same time it should hold conveniently a given volume of the fertilizer. Various factors which determine the optimum dimensions of a bag for holding 50 kg. of a fertilizer has been presented and discussed with due regard to the practical aspect of the problem. It has been shown that any drastic increase in the length/breadth ratio introduces unnecessary stresses to the bag.

An Optimum Dimension of Polyethylene-Lined Jute Bag for Packing Fertilizers

By SURENDRA MOHAN, D. K. SEN AND S. VARMA

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

The cost of the packaging material is dependent on the dimensions of the bag. By and large, 50 kg. capacity bags have been accepted as standard for packing fertilizers. The actual dimensions acceptable depend on the bulk density of the fertilizer to be bagged with provision for some free space or ullage. There are various possible ratios of length-to-breadth to accommodate a given volume of the material, and the holding capacity of a bag is found dependent on this ratio. Some interesting papers have recently appeared on the problem of optimization of the size of the bags.

Gedam, Singh and Mukherjee¹, on the basis of theoretical considerations, derived an expression involving length and breadth of the bag which was claimed to possess the maximum holding capacity with a minimum cross-sectional area of jute used. They assumed that the filled bag took the shape of a cylinder with two ends collapsed. The following relationship was developed involving the length and the breadth of the bag.

$$L = 1.9 B + 4.4 \quad (1),$$

which gave the optimum size for urea as 20'' × 43'' and 18'' × 38'' for nitrophosphate with length/breadth ratio greater than two. Parsons² observed that length (L) and breadth (B) of a bag are related to the volume of the material to be bagged, which can be given by the following equation:

$$\frac{1.012}{L} + \frac{0.772}{B} = \frac{1}{\sqrt[3]{V}} \quad (2)$$

Banerjee⁴ introduced a different set of constants in the

above equation, which according to him was in a better agreement with the experimental values.

$$\frac{1.164}{L} + \frac{0.672}{B} = \frac{1}{\sqrt[3]{V}} \quad (3)$$

Banerjee further showed that with certain combinations of length and breadth, the area of jute required is minimum and the optimum length (L_o) and optimum breadth (B_o) could be calculated by the following relationships provided the volume of the material to be bagged is known.

$$B_o = 1.344 \sqrt[3]{V} \quad 3(a)$$

$$L_o = 2.323 \sqrt[3]{V} \quad 3(b)$$

where V is the volume expressed in cu.in. and L_o and B_o are in inches. Thus, the optimum dimension of the bag gives a length/breadth ratio of 1.7.

The optimum length and breadth can also be calculated using Banerjee's method from Parsons' values. The equation (2) can be written as given below (2a). as the volume of the material to be bagged is known from the weight of the fertilizer to be bagged and its bulk density.

$$\frac{a}{L} + \frac{b}{B} = C \quad (2a)$$

$$\text{where } a = 1.012, b = 0.772 \text{ and } C = \frac{1}{\sqrt[3]{V}}$$

$$\text{or } \frac{b}{B} = C - \frac{a}{L} = \frac{CL - a}{L} \text{ and } B = \frac{Lb}{CL - a}$$

TABLE 1—OPTIMUM DIMENSIONS OF BAGS

(The figures within brackets are in inches.)

Fertilizer & Places Where Produced	Bulk Density, g./cc.	Volume of 50 kg. of Fertilizer, l.	Optimum Internal Length × Breadth		Overall Dimension of Bags*		Overall Dimensions of Bags in Use, cm. (in.)	Area of Jute Cloth		
			Parsons L/B-1.3, cm (in.)	Banerjee L/B-1.7, cm. (in.)	Parsons cm. (in.)	Banerjee cm. (in.)		Parsons, sq.in.	Banerjee, sq.in	In actual use, sq.in.
Urea (Sindri)	0.72	69.4	82.6 × 63.5 (32.5 × 25.0)	95.7 × 55.2 (37.7 × 21.1)	91.4 × 66 (36 × 26)	104.1 × 56 (40 × 22)	89 × 66.3 (35 × 26) L/B—1.3	1998	1886	1944
Urea (Namrup)	0.74	67.5	81.8 × 62.8 (32.2 × 24.7)	94.8 × 54.6 (37.3 × 21.5)	91.4 × 63.5 (36 × 25)	104.1 × 56 (40 × 22)	89 × 66.3 (35 × 26) L/B—1.3	1924	1886	1944
Urea (Gorakhpur)	0.78	64.1	80.6 × 61.8 (31.7 × 24.3)	93.1 × 53.8 (36.7 × 21.2)	88.9 × 63.5 (35 × 25)	101.6 × 56 (39 × 22)	89 × 66.3 (35 × 26) L/B—1.3	1872	1840	1944
Ammonium Sulphate Nitrate (Sindri)	0.85	58.8	78.2 × 60 (30.8 × 23.5)	90.5 × 52.3 (35.6 × 30.6)	86.3 × 61.0 (34 × 24)	99 × 53.5 (38 × 21)	89 × 61.2 (35 × 24) L/B—1.4	1750	1716	1800
CAN 25% N ₂ (Nangal)	1.05	51.0	75.6 × 57.3 (30 × 22.7)	86.3 × 50 (34 × 19.6)	86.3 × 58.5 (34 × 23)	96.5 × 51 (35 × 21)	89 × 50.8 (35 × 20) L/B—1.7	1680	1512	1584

With provision for side/bottom stitches and optimum free space

$$\text{therefore, } LB = \frac{L^2b}{CL - a} \quad (3)$$

$$\text{For the area } LB \text{ to be minimum, } \frac{\delta(LB)}{\delta L} = 0$$

and the equation (3) on differentiation leads to

$$2Lb(CL-a) - CL^2b = 0 \text{ and } L_0 = \frac{2a}{C} = 2.024 \sqrt[3]{V}$$

$$B_0 = \frac{2b}{C} = 1.544 \sqrt[3]{V} \text{ with}$$

L_0/B_0 ratio = 1.3 The optimum length (L_0) and breadth (B_0) values of the above relationships have been calculated and presented (Table 1) for various fertilizers with varying bulk densities. It is to be noted that L_0 and B_0 are the internal length and breadth of the bag.

After making corrections for the side and bottom stitches and optimum space, the results are compared with the dimensions of the bag currently in use at the

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various producing units of F.C.I.* The dimensions of the bag in actual use compare favourably with the Parsons' values corrected to give the overall dimensions of this bag, with optimum free space. Only those bags used at the Nangal unit are smaller than desirable and possess less than optimum ullage and correspond to the length/breadth ratio advocated by Banerjee on the basis of cost considerations. The length/breadth ratio of about 1.7, according to us, is inconveniently narrow, whereas the corrected overall dimensions of the bag, according to Parsons' relationship, appear acceptable from various considerations and should preferably be adopted. It is to be noted that a narrower bag would be more susceptible to damage while experiencing butt-end fall on account of reduced area of contact and increased stress concentrations on the side seam.

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[Original mss. received April 16, 1970]

The related aspects concerning the extent of protection needed by urea under widely varying climatic conditions are discussed here in the context of the inherent flexibility found in the polyethylene-lined jute-bags. Such an approach is more appropriate and is likely to result in an overall economy without affecting the quality of the product.

Packaging of Fertilizers: Optimum Protection Against Humidity

By S. VARMA, D. K. SEN, SURENDRA MOHAN AND
J. P. SINGH,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

It is necessary that the packaging cost of a relatively inexpensive commodity, like fertilizer, is kept at a minimum. At the same time, the package or bag should be able to stand the rigours of handling and protect the fertilizer from atmospheric humidity. The extent of protection from humid air needed by a fertilizer depends as much on its hygroscopic nature as on humidity and the temperature conditions prevalent where the fertilizer is produced and the region in which it is distributed. Selection of the bag on the basis of worst climatic conditions is no doubt safe but is hardly economical and is often wasteful. Need arises, therefore, to provide optimum protection on the basis of average conditions prevalent in the region served by fertilizer. This is all the more necessary in the case of polyethylene-lined jute bags as the price of jute in recent years has been increasing progressively. Such bags consist of a thin polyethylene film laminated to the jute with bitumen. The polyethylene film imparts moisture impermeability and the strength of the packaging material is due to the jute part of the bag. The role of bitumen is of an adhesive which protects the thin plastic film from getting damaged during handling. The dimensions of the bags are such that it can conveniently hold 50 kg. of the fertilizer. Such a type has been found suitable for packaging hygroscopic fertilizers.^{1,2}

In the present communication, an attempt has been made to focus the various issues involved in drawing the specification of polyethylene-lined jute bags which provide optimum protection to urea under varying humidity conditions keeping in view the limited flexibility of the

packaging material. In this context performance evaluation tests have been so evolved that the performance of a bag under high, moderate and low humidity regions can be assessed in a humidity and temperature-controlled climatic chamber.

Moisture Impermeability

The first important point worth considering in some details is to know the conditions under which a fertilizer absorbs moisture. It absorbs moisture when the vapour pressure of atmosphere exceeds that of its saturated solution. In such a situation the fertilizer, if unprotected, would go on absorbing moisture till it dissolves completely and the solution becomes undersaturated to an extent that its vapour pressure equals that of the atmosphere. Broadly speaking, the driving force of the transfer of moisture from the air to the fertilizer is proportional to $P_A - P_S$ where P_A and P_S are the vapour pressures of the atmosphere and the saturated solution of the fertilizer respectively. For convenience, $P_A - P_S$ can be expressed in terms of relative humidities $RH_A - RH_S$, where RH_A is the relative humidity of the atmosphere and RH_S the critical relative humidity (CRH) of the fertilizer³. Thus, the rate of moisture absorption is a function of the, relative humidity of the atmosphere as well as the nature of the fertilizer, as characterized by its CRH value, which varies with the temperature—decreasing normally with the increase in the ambient temperature.

For a given temperature, CRH value of a given ferti-

lizer is fixed but the relative humidity of the atmosphere varies from place to place. Even day-to-day variations in the relative humidity are noticed. For a given location, significant variations have been observed during a 24-hours period. In a recent paper while discussing air-conditioning requirement for the bulk storage of urea, cook⁴ has drawn attention to the effect of fluctuation of humidity during a day on the free-flowing characteristics of urea. From this, it is apparent that the monthly average humidity and temperature data for one-year cycle is not adequate to give necessary information regarding the behaviour of the fertilizers and the extent of protection needed. For the present, we are concerned with the bagged fertilizer where the day-to-day variation in the relative humidity and the temperature of the atmosphere are not so critical. The climatological data found adequate for our purpose are temperature and humidity values, recorded every morning, and an average value of a week is taken for a complete yearly cycle. The year in question should be free from any climatic abnormality.

Let us take urea as an example, since this fertilizer is being produced in widely varying environments, such as Sindri, Namrup and Kota, climatological data of which are available and may be taken to represent three regions which are humid, highly humid and relatively dry respectively. Instead of drawing a graph of average relative humidity of each month for one complete year cycle and super-imposing critical relative humidity of urea, as is the common practice, it may be more informative to draw $RH_A - RH_S$ for the weekly average relative humidity values for full one year cycle. RH_S values of urea or its CRH have been calculated at the temperatures recorded at these places using the following expression, derived by Piggott⁵ on the basis of experimental data.

$$\log P_s = 74.208 - \frac{5016.9}{T} - 22.679 \log T$$

From the vapour pressure of saturated urea solution, RH_S values were calculated with the help of following relationship.

$$RH_S = \frac{P_s}{P_w} \times 100$$

where P_s and P_w are the vapour pressures of saturated urea solution and water respectively at a given temperature.

From Fig. 1 it is clear that a portion of the curve is positive and another falls below the zero line. The top portion of the curve above the zero line represents the

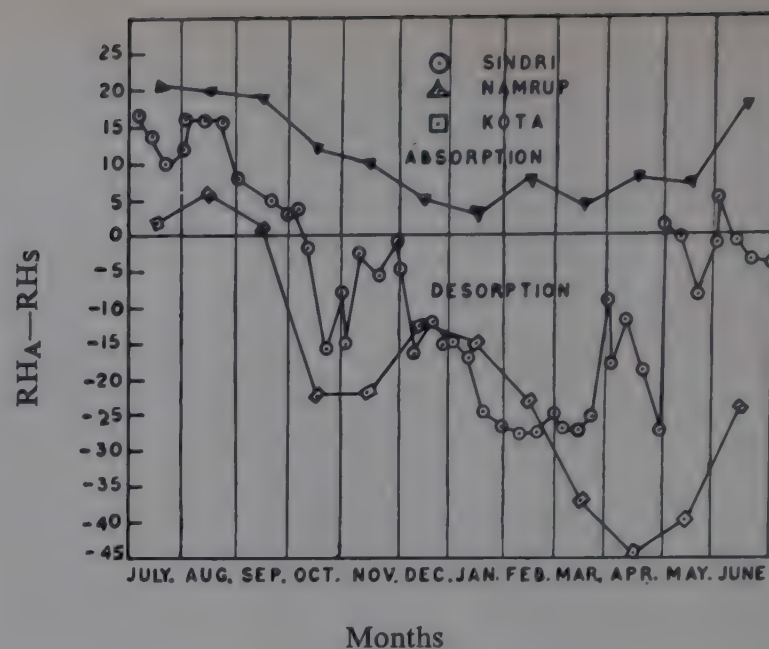


Fig. 1—Climatological Data for Urea

positive values of the driving force $RH_A - RH_S$ and urea would tend to absorb moisture during those periods. The curve below the zero line is for the negative values of $RH_A - RH_S$, where the vapour pressure of saturated solution is greater than that of the atmosphere and the fertilizer would have a tendency to lose moisture. The portion falling close to the zero line indicates that during these periods urea would neither absorb nor lose moisture.

The implication of this is that in region as humid as Namrup there will be strong and continued tendency for urea to absorb moisture throughout the year. The entry of moisture through the stitch holes as well as its diffusion through the polyethylene film is likely if the film thickness is inadequate. The fertilizer, therefore requires *Maximum Protection*. Under such an adverse condition it is advisable to use loose polyethylene-film liner of increased thickness of the order of 50 μ or above in which case, bitumen is not necessary. The mouth is tied with a cord and inserted inside the outer jute bag which is finally stitched. Alternatively, the polyethylene-lined jute bag with increased thickness of polyethylene film can be used and finally stitching done on the folded seam.

The climatic conditions at Kota are just the reverse. Only during two months in a year urea would have a continued tendency to absorb moisture. The driving force $RH_A - RH_S$ is, however, small. In such a situation thickness of the polyethylene film can be reduced to about 25-30 μ and there would not be any significant diffusion through the stitch-holes even during humid months since the rate of moisture uptake would be slow and the deep penetration of moisture is unlikely in view of absorption and desorption occurring at frequent

intervals. Urea produced and distributed in a low humidity region, close to Rajasthan, would thus require *moderate protection*.

At Sindri and its adjoining areas urea would have a continued tendency to absorb moisture for nearly four months in a year. The moisture penetration has been found to occur only through the stitch-holes during the monsoon period and becomes significant only on continued exposure of the bag to a high humidity. Moisture diffusion through the film free from pin holes has been found to be insignificant provided the thickness is of the order of 40 μ . In such a climatic condition urea requires *adequate protection*. It is significant to note that the cost of polyethylene film depends on its thickness. A saving of 20 paise in each bag using reduced thickness of polyethylene film for moderate protection amounts to a saving of over one million rupees every year for a plant producing 1000 tons of urea a day without any adverse effect on the quality of the product.

Performance Evaluation Tests

The atmospheric humidity conditions have been characterized according to the protection needed to urea, viz. maximum, adequate and moderate. It is significant to note that the temperature conditions maintained for the accelerated test in the climatic chamber are higher in the case where more protection is needed. This has been done for two reasons, firstly because CRH value of urea is lower at higher temperature thereby increasing the value $RH_A - RH_S$, and secondly the rate of absorption coefficient also changes.

(i) *Maximum Protection (High Humidity)*: A single layer of bags placed widely apart were subjected to a relative humidity of 95 per cent at 45°C for a period of about 350 hrs. in a humidity and temperature controlled climatic chamber. Samples were taken out from the

inside near the top exposed face and also from the portion near the mouth. The performance of the bag was considered satisfactory when the amount of moisture increase in urea in the interior as well as near the mouth was of the order of 0.1 and 0.2 per cent respectively.

(ii) *Adequate Protection (Average Humidity)*: The bags placed as above were subjected to a relative humidity of 90 per cent at 40°C for a period of 350 hrs. The bags were considered satisfactory if the moisture increase in the interior as well as near the mouth did not exceed 0.1 and 0.2 per cent respectively.

(iii) *Moderate Protection (Low Humidity)*: The qualifying test for moderate protection consisted in exposing the bags to a relative humidity of 80 per cent for a period of 300 hrs. at 30°C. The bags were sufficiently moisture-proof if the moisture increase was of the order of 0.1 and 0.2 per cent in the sample taken near the mouth and near the top face respectively.

Attempts have, however, been made from time to time to revise the specification of the bag to keep down the packaging costs. This has mostly been done without giving due consideration to the issues involved. The situation now is different with increased availability of urea and the manufacturers would have to ensure that the product supplied is free-flowing.

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The chafer beetle, *Adoretus duvanceli*, is an important pest of grape vine in India. This pest remains inactive under the soil surface during the day and becomes active during night and feeds on the leaves of the crop. Due to its peculiar feeding behaviour the usual method for controlling it proved less effective. Therefore, an attempt has been made here to find out some resistant varieties which can be successfully utilized as breeding material for this purpose.

Studies on the Relative Susceptibility of Different Varieties of Grape to *Adoretus Duvanceli* Blanch

By D. P. CHAKRABARTY, G. C. GHOSH, P. K. DAS
AND S. P. DHUA,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

One year old potted plants of 21 varieties of grape were obtained from the Horticulture section of this Division of FCI Ltd. and the natural infestation by the pest, *Adoretus duvanceli*, was recorded at the peak period. The infestation was graded as low and high according to the intensity of damage under visual observation. The leaves having more than 15 per cent damage were grouped under 'high' type and less than that were grouped into 'low' type damage. Out of these 21 varieties tested under natural condition, 8 varieties were selected from three types, like resistant, intermediate and susceptible, and subjected to artificial infestation by caging one starved beetle in each variety for 24 hours. This was replicated thrice. The variety, Pusa Seedless, which has gained much popularity, was also included in this trial. The area of the leaves eaten by each beetle was measured and recorded. Afterwards these varieties were analysed for their moisture and nitrogen content in order to find out the cause of resistance.

Results: Field Study

High and Low Type Damage: The varieties differ significantly in both the types of damage. In the high-type damage the least infestation was observed in the variety, Bangalore Blue, closely followed by in Jaisi. The highest damage was observed in Charas and differ significantly from all other varieties. Others were in the intermediate group.

In the low-type damage, the lowest value was obtained in Bangalore Blue followed by in Gujranwala, Bhokri, and Perlette. The highest damage was obtained in Gulabi followed by in Hemrod, Black Prince, Foster's Seedling and Mukchalani. Others were in the intermediate group.

Overall Damage: The highest damage was obtained in Charas closely followed by in Black Prince, Gulabi, Mukchalani and Pearl of Csaba. The lowest damage was obtained in Bangalore Blue followed by in Bhokri, Jaisi and Perlette. Other varieties were in the intermediate group.

Cage Study: The highest value was obtained in Gulabi closely followed by in Perlette, Black Prince and Pusa Seedless. The lowest infestation was obtained in the variety Bhokri with no significant variation with Bangalore Blue.

Moisture and Nitrogen Percentage: The maximum moisture percentage was obtained in Pusa Seedless followed by in Gulabi and Perlette. The minimum was in Madeleine Angevine and Bharat Early.

The maximum nitrogen percentage was obtained in Bharat Early and the minimum was in Black Prince followed by in Pusa Seedless and Pearl of Csaba.

Discussion

A. duvanceli is one of the serious pests of grape. Wadhi and Batra¹ reported that this beetle along with others

TABLE 1—MEAN PERCENTAGE (TRANSFORMED VALUE) OF LEAF DAMAGE AND MEAN AREA CONSUMED BY THE BEETLE, *Adoretus duvanceli*, IN DIFFERENT VARIETIES OF GRAPE

Sl. No.	Variety	Field Study			Cage Study
		Mean Percentage of a Low type Damage	Mean Percentage of a High type Damage	Overall Damage	Mean Area Consumed by Each Beetle in 24 hr., sq.mm.
1.	Bangalore Blue	8.81	6.66	7.74	81.00
2.	Bharat Early	16.49	21.13	18.81	144.33
3.	Black Prince	19.36	27.67	23.51	188.00
4.	Madeleine Angevine	13.11	22.88	18.00	114.33
5.	Gulabi	22.06	23.14	22.60	194.67
6.	Bhokri	8.17	9.54	8.86	54.67
7.	Pearl of Csaba	13.23	27.33	20.28	121.67
8.	Parlette	9.31	13.86	11.59	188.67
9.	Pusa Seedless	—	—	—	186.33
10.	Gujranwala	12.79	14.73	13.76	C.D. at 5% 29.26
11.	Banquibad	14.04	18.12	16.08	—
12.	Hur	17.71	19.73	18.72	—
13.	Foster's Seedling	18.78	20.43	19.61	—
14.	Jaisi	13.18	8.01	10.59	—
15.	Dutch Sweet	17.36	12.18	14.77	—
16.	Sadipur Local	16.24	19.87	18.05	—
17.	Mukchalani	17.97	22.71	20.34	—
18.	Sapirabi	16.33	23.01	19.67	—
19.	H.K. Bell	12.38	15.64	14.01	—
20.	Charas	16.35	32.88	25.87	—
21.	Muscat Oliver	16.42	18.35	17.39	—
22.	Hemrod	19.52	17.65	18.58	—

C.D. at 5% for treatment means 4.11

C.D. at 5% for overall means 5.81

cause noticeable damage to grape. In an attempt to find out the less susceptible variety from the existing varieties on trial, Bangalore Blue and Bhokri have shown some resistance to this pest in natural condition. The cage study also confirmed that these are not cases of 'escape' from the damage but may contain some resistant factor as the quantity of leaves consumed was significantly less than in the others (Table 1). The varieties, like Black Prince and Charas, were observed to be in the susceptible side and require much attention to protect the crop from the Chafer damage. The variety, Pusa Seedless, was also observed to be much susceptible under cage condition. Bangalore Blue is the natural hybrid of *vinifera* and *labrusca*. It may be possible that one of the parents might have contributed this resistant factor.

The moisture and nitrogen percentage could not give any indication for the cause of this resistance. Further work on the chemical aspect, like sugar and silica content of the leaves, may throw some light on the cause of this resistance.

TABLE 2—MOISTURE AND NITROGEN PERCENTAGE OF THE LEAVES OF DIFFERENT VARIETIES OF GRAPE

Sl. No.	Variety	Moisture in the Composite Sample, %	Nitrogen in the Composite Sample, %
1.	Bangalore Blue	71.79	3.14
2.	Bharat Early	69.56	3.88
3.	Black Prince	72.30	2.80
4.	Madeleine Angevine	68.33	3.31
5.	Gulabi	76.66	3.14
6.	Bhokri	72.58	3.25
7.	Pearl of Csaba	71.42	2.91
8.	Perlette	75.34	3.31
9.	Pusa Seedless	80.23	2.91

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The present knowledge of gravitation is summarized and then it is shown with documentary evidences that the Hindu mathematicians and philosophers developed the concept of universal gravitation much before Newton and that they, in unequivocal terms, mentioned about the earth's gravity and the universal gravitational field in their writings in ancient times.

On Universal Gravitation*

INDU SEKHAR MISRA,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Historical Background

The systematic and meaningful astronomical developments which led to the establishment of the theory of gravity and finally the universal gravitation itself started with the concept of Nicholas Copernicus (1473-1543) re-establishing the antique postulate of uniform circular motion of planets round the Sun—the so-called heliocentric theory. Copernicus thought the Sun to be occupying the central position of the universe round which he supposed the then five known planets including earth revolving in roughly circular orbits, each having its own characteristic period. He further assigned to the earth a daily axial rotation to account for the rising and settings of the heavenly bodies. His historic book, *De Revolutiones Orbium Coelestium Libri VI*, was published in 1543 and the same year he died.

Later, E. Reinhold published in 1551 the table of celestial movements following calculations based on Copernican principle, but this table was found to be defective because it showed large deviations from the observed celestial positions and so Landgrave William IV (1532-1592) and the Danish astronomer, Tycho Brahe (1546-1601), studied the celestial movements by refined methods. For this purpose the first revolving dome observatory was built by Landgrave at Cassel in 1561.

*This paper is dedicated to the memory of the great and perhaps the first astronomer of the world, Aryabhatta of *Pataliputra* (modern Patna), whose birth anniversary is celebrated on the 13th April every year.

He worked on his instrument for many years but finally left it incomplete. On the other hand, Tycho Brahe's works were of comprehensive type and accurate but instead of accepting Copernican planetary theory, he developed his own in which the planets revolved round the Sun while the Sun and moon revolved round the fixed, central Earth.

After Tycho Brahe's death, his German assistant Johann Kepler (1571-1630), a Copernican, utilized former's observations of Mars and was led to state his first two laws of planetary motions in his celebrated *Astronomica Nova* in 1609. The laws are: (i) Each planet moves around the Sun in an ellipse, with the Sun at one focus; (ii) the radius vector from the Sun to the planet sweeps out equal areas in equal interval of time.

Kepler announced his third law in 1619 in his *De Harmonice Mundi* as: The squares of the periods of any two planets are proportional to the cubes of the semi-major axes of their respective orbits i.e. $T \sim a^{3/2}$.

Simultaneously, Galileo Galilei (1564-1642) with his telescope was scanning the sky and making great astronomical discoveries, such as the mountainous irregularities on moon's surface, the four principal satellites of Jupiter, the Milky Way's luminosity being an aggregation of innumerable faint stars, and the demonstration and measurement of the axial rotation of the Sun, etc. Fortunately, Galileo's discoveries were in tune with Copernican cosmology which he described in his historic *Dialogue on the Two Chief Systems of the World* (1632).

The Law of Gravitation

After the establishment of the Copernican concept that planets revolve round the Sun the most puzzling question at the time was how and with what motion these planets went round the Sun and also from where did the force causing planetary rotation originate? One of the theories at the time was that there were many invisible angels who beat their wings constantly and thus drive the planets round the Sun. But contemporary scientists did not believe this unscientific concept and therefore their search for the real cause continued. In the mean time, Galileo proposed a brilliant idea—the principle of inertia—that “if something is moving with nothing touching it and completely undisturbed, it will go on moving for ever, coasting at a uniform speed in a straight line”. Galileo did not mention what causes change in movement (motion) to a body. It was Newton who stated that it is only a force which changes the magnitude and direction of a body's motion. He also stated that an acceleration produced by a force is inversely proportional to the mass of the accelerated body, that is the applied force is proportional to the product of mass and acceleration.

Newton discovered earth's gravity from the fall of an apple and from Kepler's second law that planets sweep out equal areas in equal time, he concluded that all of the planetary forces are precisely directed towards the Sun. From the then known astronomical fact that the planet Jupiter had moons moving round it in the same manner as our own moon went round the earth, he proposed the concept of a universal force that everything pulls everything else. This pull is directed towards the common central position of all the moving planets and satellites such that each of these goes round this central position.

Newton, thus, stated that the force of attraction between any two planets are: (i) directly proportional to the product of their masses, and (ii) inversely proportional to the square of the distance between them.

$$\text{Thus } F = G \times \frac{m_1 m_2}{r^2} \quad (1)$$

where G is constant, called by Newton the universal constant. This G has a value equal to 6.67×10^{-8} in CGS units. This means if two masses each of one gram are 1 cm apart, the mutual force of attraction between them would be 6.67×10^{-8} dynes.

Einstein's Theory

Einstein, when applied his theory of relativity to

Newton's theory of gravitation, found the latter incorrect in some respect and so modified it accordingly. He argued that no signal can travel faster than the velocity of light in vacuum and hence Newton's concept of instantaneous gravitational effect which necessarily means that signals can be faster than c must be changed. He had earlier in 1905 established the concept of equivalence of mass and energy (his famous equation $E = mc^2$) and in 1916 predicted in his general relativity theory that light rays in space while passing through a gravitational field would be deflected in the direction of the gravitational pull. This was found true during Sun's total eclipse in 1919 by Arthur Eddington. Einstein's gravitational theory also proved that gravity influences all physical systems and affects their process rate, such as a time-piece will go fast on the surface of the Sun where the gravity is very strong compared to the earth's surface where the same time-piece will go slow because of the weaker gravity of earth.

The far-reaching consequences of Einstein's theory is the concept of a curved space and time caused by the presence of gravitating masses and that any motion in this space takes place along the “Straightest” (geodesic) lines. That is, the presence of masses in certain region of space and time provides it geometrical properties which in its turn determine the movement of masses within that space and time. Einstein's gravitational equation is given as:

$$R^{\mu\nu} - \frac{1}{2} g^{\mu\nu} R = -\chi T^{\mu\nu} \quad (2)$$

where χ is a constant and its value is determined by $\chi = 8\pi\gamma/c^2$ where γ is Newton's constant G in the equation (1). $R^{\mu\nu}$ is curvature tensor and vanishes when there is no gravitational field.

R is scalar curvature and an invariant of $R^{\mu\nu}$ which also vanishes in the absence of gravitational field.

$T^{\mu\nu}$ is mass tensor which causes the gravitational field. If $T^{\mu\nu}$ is zero everywhere in a certain region of space and time then the gravitational field would be absent in that region of space and time. $g^{\mu\nu}$ is metric tensor having asymptotic form and has Euclidean character at infinite distances. At finite distances it must possess the properties explained by Riemannian geometry. Thus, Einstein's gravitational equation becomes Newtonian at infinite distances from the origin of the gravitational wave, but for a finite distance it does not have Newtonian character but deviate slightly due to curvature of space and time caused by the presence of gravitating masses concentrated in certain region of space and time and must not be distributed uniformly throughout space. But later in 1922, A. A. Friedmann reached to the con-

clusion, after solving Einstein's gravitational equation that space is isotropic and there is a uniform mass density distribution throughout this isotropic space which confirmed the earlier theoretical assumption of distribution of matter (pressure less dust) in universal space.

Studies in Ancient India

After having summarized briefly our present knowledge of gravitation developed since Copernicus, we now go back to the olden days and recall the concept of gravitation enunciated by Hindu mathematicians and philosophers.

A verse in the famous *Suryasiddhanta* reads as:

मध्ये समन्तादन्डस्य भूगोलो व्योम्नि तिष्ठाने ।

विभ्राणः परमाशक्ति ब्रह्मणो धारणालिकाम् ॥

Suryasiddhanta

(In the centre of the universe, in the sky, earth which is spherical from all the four sides and which has inhibited attracting force from the creator of the universe, is situated. That is, earth is having attracting power.)

The exact timing of *Suryasiddhanta* is not known and is controversial but Varahmihir in his treatise *Panchsidhantika* in A.D. 507 has described the subject of *Suryasiddhanta* and therefore *Suryasiddhanta* must be before A.D. 507

Bhaskaracharya in 1160 A.D. had stated in his treatise *Siddhanta Shiromani*:

यथोष्णताकनिलयोस्तु शीतता विधौद्रुतिः के कठिनत्वमश्मनि ।

मरुञ्चोभूश्चला स्वभावतो यतो विचित्रावत वस्तु शक्तयः ॥

आकृष्टिशक्तिश्च महीतया यत् स्वस्थंगुरु स्वाभिमुखं स्वक्तया ।

आकृत्यते तलततीव भाति समे समन्तातक्व पतित्वियं स्वे ॥

Siddhanta Shiromani, Goladhyaya

(It is evident that the Sun and fire are hot, moon is having coolness, water is having flow, stone is hard, and wind blows. Similarly, earth is static because material force (or energy) is having peculiarities. Earth has gravity and any matter (having a weight) in the sky is attracted towards it and that body appears falling. But as regards earth, it is surrounded by sky (space) identically from all sides and therefore where should it fall.)

Commenting further Bhaskaracharya wrote:

आकृष्टिशक्तिश्च महित्येनन् भूमेरधः पतनं तत्तियगधः स्थितानां

याधः पतनशंका निरस्ता ।

(There is gravity in earth and therefore the falling of earth, and the question of falling of people living on its upper as well as lower surfaces was solved.)

This was said by Bhaskaracharya in reply to a query by Buddhist philosophers. In those days Buddhist philosophers had a concept that the people residing on the upper surface of earth should feel the people living on its lower surface falling.

The great astronomer Aryabhatta, in his one of the oldest books or probably the oldest book on astronomy—*Aryabhateeya*, wrote in A.D. 499

वृत्तभपञ्जरमध्ये कक्षापरिवेष्टितः स्वमध्यगतः ।

मृज्जलशिखिवायुमयो भूगोलरसर्वतो वृत्तः ॥

(In the centre of the circular orbits of moon and planets, surrounded by sky consisting of atmosphere of fine dust of matter, water and fire the spherical shaped earth is located. Thus, by saying that earth is in the centre of sky (space) from all sides is enough to clear that earth stationed as such is due to its own force—the *gravitational force*.)

Similarly Brahmagupta too, in his treatise *Brahmasphut Siddhanta* in A.D 608., had stated:

इवेभूगोलस्तदुपरि मेरो देवाः स्थितास्तले दैव्याः ।

Brahmasphut Siddhanta

(Earth is spherical in the sky and on its upper surface on *Meru Hill* there are different gods while on its lower surface monsters are living. That earth is spherical in the sky is sufficient to mean that earth is stationed in the sky due to its own force.)

Shri Pani Bhatt, in his treatise *Siddhanta Shekhar*, had wonderfully explained the gravitational force of earth and the concept of universal gravitation caused by the other heavenly bodies in A.D. 1037 He said:

नभस्य यस्कान्त महामर्णतनां,

मध्ये स्थितो लौहमुडो यथाऽऽस्ते ।

आधार शून्योऽपि तथैव सर्वा,

धारो धरित्या ध्रुवमेव गोलः ॥

Siddhanta Shekhar

(Earth, even without any base, is there in the static sky (space) which may be thought of acting as base for all heavenly bodies, is surely spherical and it experiences physical forces similar to an iron ball surrounded by magnets from all sides.)

The concept of earth's gravitation had been initially mentioned in the *Vedas*. The period of the *Vedas* is thought to be about ten thousand years ago. The well-known Sutra of the *Yejurveda* says:

आयं गौः पृश्निरक्रमीद सदन्मातरं पुरः ।

पितरं च प्रयन्स्वः ॥

Yejurveda, Chapter 3, Verse 6

(The spherical earth goes round the Sun together with water on its surface and therefore earth moves)

Another famous *Sutra* of the *Atherveda* describes the concept of universal gravitation in the following way:

आकृष्णेन रजसा वर्तमानो निवेशयन्नमृतं मर्त्यं च ।

हिरण्ययेन सविता रथेन दैवो याति भुवनानि पश्यन् ॥

Atherveda, Chapter 33, Sutra 43

(The Sun, which is the creator of rain; which is having intense light and is bright and lovely moves on its axis with all the living and non-living ones after transfusing into them nectar like rain and light, and taking all matter and all planets with it, after having established a gravitational pull with each of them. But it does not move round any planet. Likewise each universe is having its own Sun which gives light to all of its matter and planets. There are many such universes)

A second Sutra in *Atherveda* Says:

दिवि सोमो अधिश्चितः ॥

(The moon is lighted by the Sun)

Atherveda, Kanda 14, Chapter 1, Verse 1

Thus, we can clearly infer from some of the aforesaid Sanskrit Sutras how deep and excellent concept of gravitation was developed by Hindu mathematicians

and philosophers in the ancient times. Although they were mathematically not precise or at least little is known about their mathematical precision in regard to gravitation, yet their ideas and concept can certainly delight us and lead us to a deeper understanding of the physical universe.

Acknowledgements

The author expresses his gratitude to Acharya Baldev Mishra, one of the most celebrated scholars on Indian mathematics and astronomy and the writer of the famous *Aryabhattiyam*, for arousing his interest in Hindu astronomy and subsequently providing the first six Sanskrit *Sutras*. He is also grateful to Pandit Dinanath Jha for many valuable discussions on antique scientific postulates regarding the universe and its evolution developed in the ancient India. Shri N. P. Mishra of the Chemical Research Wing, P & D Division, has provided the author with the last three Sanskrit *Sutras*.

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[Original mss. received on Feb. 10, 1970]

THE PROCEEDINGS OF THE SEMINAR ON WASTES AND EFFLUENTS IN CHEMICAL INDUSTRIES HELD AT THE SINDRI UNIT OF F.C.I. LTD. HAVE BEEN PRINTED AND ARE AVAILABLE FOR SALE

Contains 29 papers on diverse aspects by leading authorities and specialists. The papers provide a valuable survey on the problem of industrial effluents and the possibilities of their treatment and disposal in India. (103 pages). Enquiries may kindly be made with the Editor, TECHNOLOGY.

Price : Indian Rs. 7.00 (excluding postage); Foreign \$ 2.50 (including Sea Mail postage; Air Mail charges extra)

The conventional quartz spring balance has been modified by introducing a simple inert gas counter-flow device for studying surface reactions of catalytic conversion of carbon monoxide in steam-gas flow systems. This device prevents any upward convectional draught and thus prevents condensation of vapours in the upper region of the balance.

A Modified Spring Balance for Studies on Catalytic Conversion of Carbon Monoxide in Steam Gas Flow System

S. R. NAIDU, G. SENGUPTA, D. K. GUPTA & S. P. SEN,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Suspension-type quartz spring balance has been used by several workers for gravimetric gas adsorption measurements. However, studies involving condensible vapours, e. g. steam, naphtha, etc., at vapour pressure higher than that at room temperature, present certain difficulties, such as condensation of vapours in the upper region of the balance. Elaborate arrangements are, therefore, needed to keep whole of the balance housing at temperatures sufficiently high in order to prevent condensation. This results in an undesirable stretching of the spring and the balance has to be calibrated for each operating temperature. Moreover, there is little evidence of such balances being used in flow systems.

Similar difficulties were encountered by the present authors while studying surface reactions of catalytic conversion of carbon monoxide in steam-gas flow systems. Therefore, in the conventional quartz spring balance a simple inert gas counter-flow device was introduced which prevented any upward convectional draught, thereby preventing condensation of vapours in the colder regions of the balance housing.

Instrument

A detailed sketch of the instrument is given in Fig. 1. Saturator is kept at a suitable temperature to get the desired steam-gas ratio, and the reactant gases, viz. carbon monoxide, nitrogen and hydrogen, etc., are passed through it. Flow rates up to 5 l./hr. have been used in the balance without causing severe oscillations

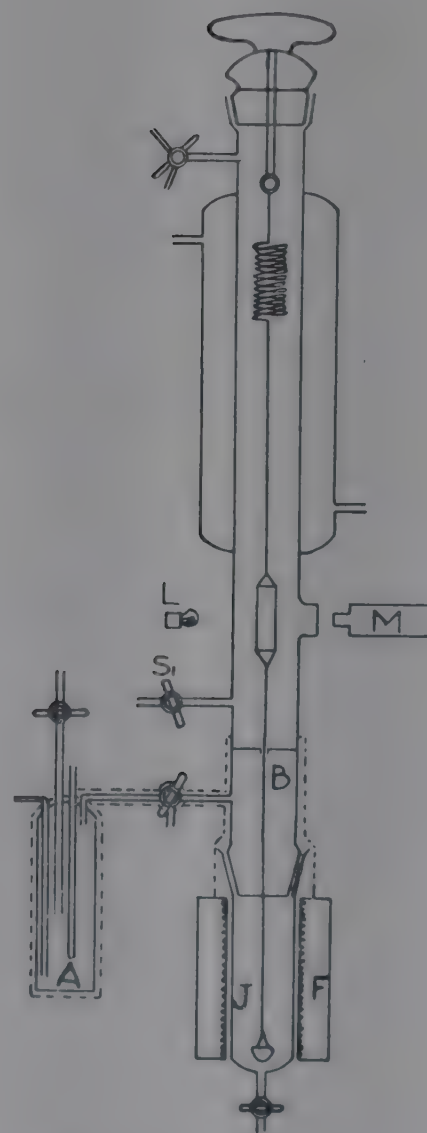


Fig. 1—Modified Balance

in it. A counter-current flow of dry nitrogen through stop-cock S¹ and baffle B prevents the upward carry-over of steam. Absolutely no moisture could be detected in the upper part of the balance housing.

The balance has been tested for stability in vacuum, in air at atmospheric pressure and in a current of nitrogen at room temperature and also at 400°C. No measurable change was observed in changing over from static to dynamic condition or from atmospheric pressure to vacuum at either temperature. Fig. 2 shows the calibration curves for the balance in vacuum and at atmospheric pressure. It can be seen from Fig. 1 that only the lower portion of the jacket J is inside the furnace and is kept at reaction temperature. By using metallic or quartz tube reaction jackets instead of pyrex glass, high temperature reactions, viz. steam-naphtha or steam-methane reformation, can also be studied.

Acknowledgements are due to Sarbasri H. N. Chakravorty and M. M. Saha for their valuable help in fabricating the instrument.

[Original mss. received on Feb. 20, 1970]

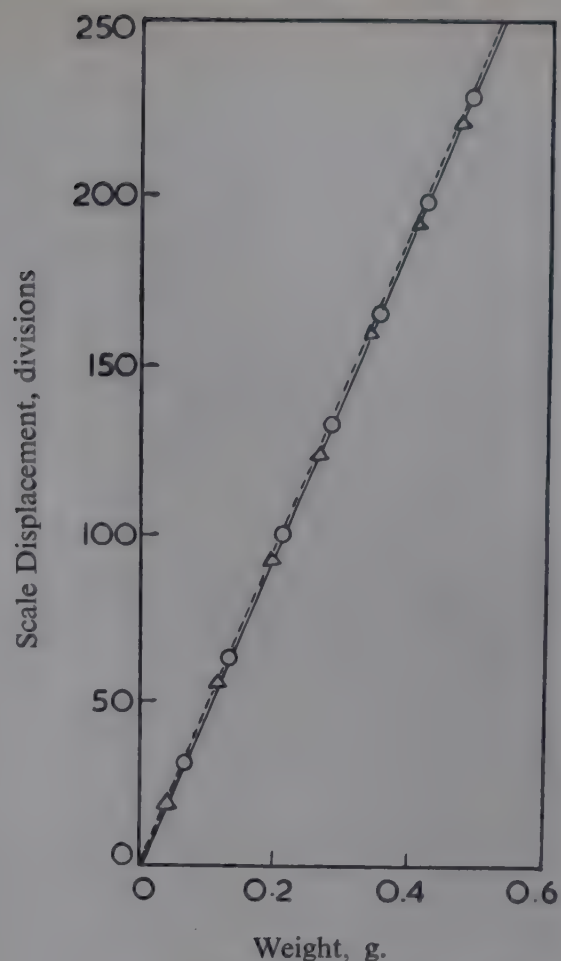


Fig. 2—Balance Calibration Curve

(Continued from page 192)

3-weeks' training programme in the laboratories of the American Instrument Co. at Silvan Spring, Maryland, on the operation and maintenance of high pressure porosimeter and Adsorptomat. The former is a versatile instrument, particularly suitable for catalyst development work. It is capable of determining the size and size distribution of pores in catalysts and other solids as small as 30Å diam. Their 60,000 psi porosimeter incorporates a fully automatic pumping system with

continuous pressure cycle and a mechanical dual gauge linear read-out system.

Adsorptomat is used extensively in investigations of porosity and surface area measurements of catalysts.

Sarbasri Ganguli and Puri visited Aminco's super-pressure plant and their assembly plant at Savage, 17 miles away from Silvan Spring.

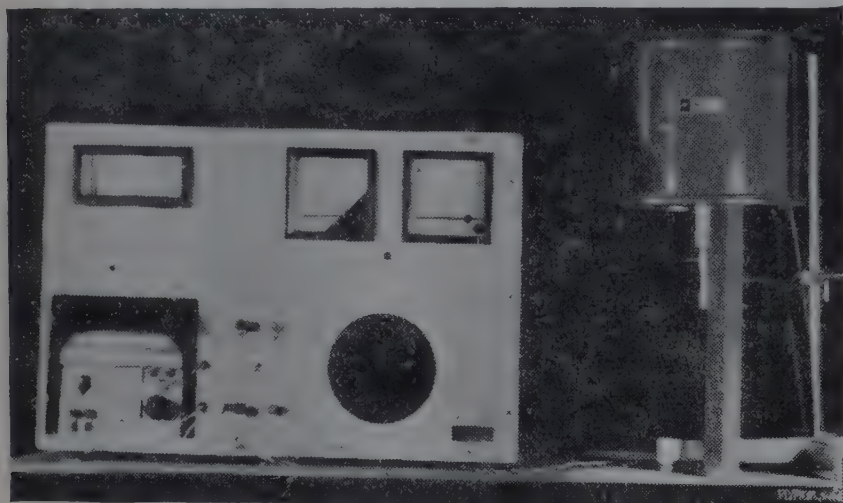
Differential Thermal Analyzer Developed at P & D Division, FCI Ltd.

The Physical Research Wing of the Planning and Development Division has developed and released for sale a DTA instrument complete with its accessories fabricated entirely from indigenous parts. A highly sensitive precision instrument, its main application is in the identification and evaluation of catalyst, identification of components in pesticides and insecticides and minerals in ores and cores, and in the determination of transition, melting and degradation reactions of plastics and fibres, stability and purity determination of chemicals and firing reaction and quality assessment of

glass and ceramics and ignition points, preignition reactions and state of oxidation in rocket, atomic and other fuels, etc.

This instrument comprises a vertical furnace which can be heated up to 1000°C at controlled rates—5 to $15^{\circ}\text{C}/\text{min}$ —by a manually operable variac connected to a 220 V 50 cycle A.C. main. The input voltage and current are measurable by a voltmeter and ammeter provided in the circuit. The measuring head comprises ceramic base with platinum sample-holders and chromel/alumel thermocouples. The instrument is provided with a highly sensitive spot galvanometer with variable sensitivity adjustment and a suitable temperature indicator for measuring differential e.m.f. and furnace temperature respectively. Accessories fitted with measuring head for maintaining different gas atmospheres (such as nitrogen) around the samples inside the furnace are also provided.

This development has not only saved valuable foreign exchange but also brought down the cost of the instrument considerably. Our instrument has already been sold to the Agricultural Research Institutes at Ranchi and Sabour, where it is being utilized successfully for research work and routine analyses.

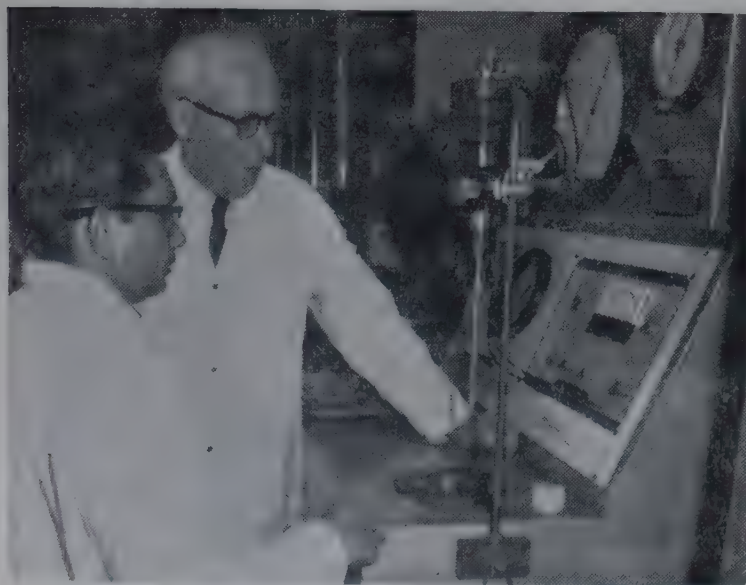


DTA Apparatus Developed at P & D Division, FCI Ltd.

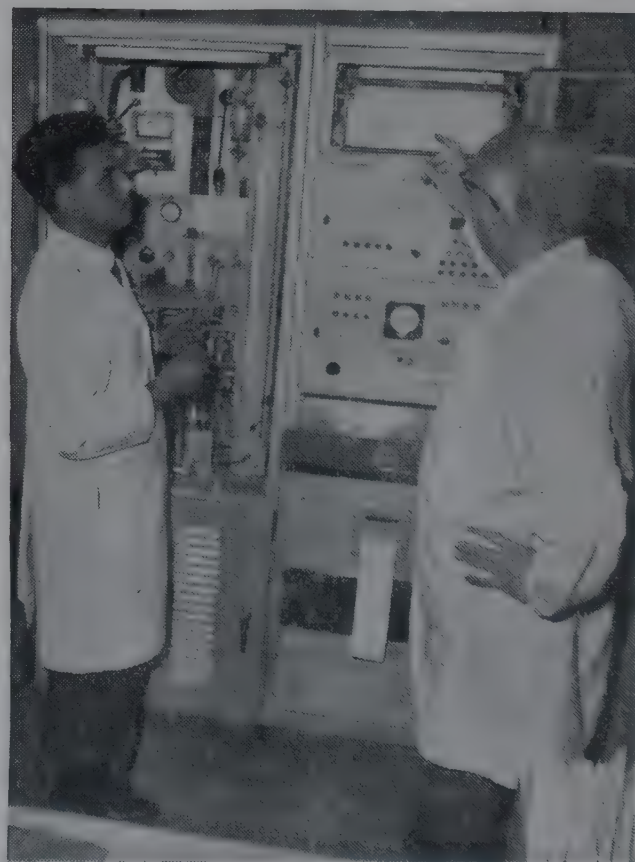
Deputation

Sarbasri N. C. Ganguli, Asstt. Superintendent, and V. K. Puri, Technologist of the Catalyst section (Chemical Research Wing), Planning & Development Division, had been to USA during April 1970 on a

(Continued on page 191 bottom)



Sri V. K. Puri with Mr. Howard in the Aminco Laboratory



Sri N. C. Ganguli (left) with Mr. Michael Howard, Director, Aminco Laboratory with Adsorptomat

Technical Digests

Effluents from Fertilizer Industries

With the growth of industrialization and urbanization, the problem of water pollution is becoming serious. Due to a variety of reasons it has not been possible to provide adequately proper treatment of wastes and effluents with the result that increasing amount of untreated sullage is polluting the water sources; even the atmosphere is getting polluted with smoke, dust and poisonous gases. While industrial expansion has received impetus, the treatment of industrial wastes has mostly gone by default in this country.

However, in recent years the need for abatement of water and air pollution and other insanitary conditions is getting well recognized. There are several permanent institutions, viz. the Public Health Engineering Research Institute (CSIR), All India Institute of Hygiene and Public Health, Indian Council of Medical Research, etc., which are tackling the problem from different aspects. The Indian Standards Institution also took steps 6-7 years ago by way of formulating standards* for (i) inland surface waters subject to pollution and (ii) industrial effluents discharged into inland surface waters, which unfortunately are not mandatory. Even in the Indian Factories Act, provisions are there for factories to obtain prior approval for the disposal of their effluents from the public health and municipal authorities and the Inspectorate of Factories.

The Government of India are also much concerned about the increasing menace of water pollution. They set up an expert committee in 1962 under the chairmanship of the well-known public health engineer, Sri N. V. Modak, to study thoroughly the available materials and make recommendations for drawing suitable enactments for prevention and control of water pollution for domestic as well as industrial wastes.

The Sindri fertilizer works, being the first major industrial enterprise of the Indian Government, is very much alive to the effluent disposal problem since its very inception. Our scientists have been successful in

reducing the pollutorial load on river Damodar and developing methods of recovery of chemicals from this factory's effluent. Foreseeing the need for extensive and all-out efforts for the disposal of wastes and effluents and undertaking researches on the recovery of chemicals from them, this Division and Sindri Unit of FCI Ltd. jointly organized a seminar on Wastes & Effluents in Chemical Industries on May 2-3 1965, wherein 29 papers covering different aspects of wastes disposal problems in various disciplines were presented and discussed.

During the last 5-6 years, several new fertilizer works and petrochemicals complexes have come up and many more will be coming during the 4th plan and after. By the end of the 4th Plan, India would be producing about 3 million metric tons of urea which would account for about 60 per cent of the total nitrogen production; so the problem of disposal of effluents from fertilizer industry would be a tremendous one. In a paper presented** at the Seminar on Water Pollution and Industrial Waste Treatment held at Bangalore during Dec. 13-14, 1969 under the joint auspices of The Institution of Engineers (India), Central Public Health Engineering Research Institute, Indian Council of Medical Research, The Indian Institute of Sciences and several Mysore Government institutions, the authors have discussed the principal effluent streams emanating from (i) nitrogenous and (ii) phosphatic fertilizer plants and their treatments. Like other heavy chemical industries, fertilizers too consume huge amount of water, a substantial part of which after use and reuse in every unit operation involved goes out as effluent streams, some of which are quite innocuous and fit for direct disposal to sewers while others contain highly toxic materials and would, therefore, require an elaborate treatment procedure before disposal. Most of the fertilizer effluents, except some of those from nitrogenous plants, can be treated by the conventional methods.

Effluents from Nitrogenous Fertilizer Plants: When

*Prior to ISI standards, the Royal Commission standards of UK were followed which had no relevance whatsoever to the Indian climate and various other conditions.

**Treatment and Disposal of Effluents from Fertilizer Industries by G. S. Roy, G. S. Bhattacharyya and B. K. Dutta, P. & D. Div. FCI. Ltd

urea is the fertilizer, ammonia is allowed to react with carbon dioxide under suitable pressure and temperature and the reacting mass concentrated, evaporated, crystallized, centrifuged and dried in the usual way. Urea plants give out mainly two types of effluents, viz. (i) one emerging from compressor house containing some oil; (ii) other more voluminous, emerging from urea concentration unit containing high concentration of ammonia and urea. The oily effluents from CO₂ compressor is treated by a conventional method of oil separation and recovery.

From factories producing ammonium sulphate, ammonium nitrate, double salt and diammonium phosphate, acidic effluent streams would emanate from the acid plants. These acidic effluents are taken care of in conventional neutralizing pits along with other acidic and alkaline effluents containing free ammonia and ammonium salts. From ammonium sulphate plant utilizing gypsum process emanates a more voluminous effluent containing some finely divided chalk particles in addition to ammonia and ammonium salts.

As tolerance for ammonia nitrogen in receiving waters is very small—1-2 and 5-10 mg./l. being limits for pisciculture and human/livestock consumption respectively—adequate steps are necessary for its removal from effluent. From consideration of economics also drainage of nitrogen should be minimized for which chemical methods of treatment are of limited use. However, biological treatment like nitrification and denitrification in the modified activated sludge process can remove ammonium, oxidized and organic nitrogens or urea satisfactorily but demand for organic carbon in the process is too high to make the process economically viable.

From the aspect of recovery of nitrogen, the biological process involving algae culturing seems more attractive due to the fact that algae can utilize nitrogenous fertilizer materials both autotrophically or heterotrophically in presence of solar energy and convert the nitrogen into protein-rich algal cells which are recoverable by suitable methods of harvesting. The harvested algae can be used as animal feed. The limitation in this biological process too is supply of adequate amount of carbon which is about 10 times the nitrogen to be removed as a substantial portion of the carbon supply would be lost in the process; moreover, utilization of nitrogen by algae being dependent on light, the surface area required for would be quite large. The capital cost involved would be comparatively high but proper utilization of the product—protein-rich algae cells as cattle feed—would counter-balance the investment.

Effluents from Phosphatic Fertilizers Plants: The

principal effluents stream emanating from fertilizer plant contains rock dust, silica, fluosilicic and phosphoric acids. This stream is combined with the effluent streams from acid plants and treated by lime in the same lagoon or neutralizing basin. By lime treatment the acidity of the effluent is neutralized, phosphoric acid is precipitated as insoluble tricalcium phosphate, fluosilicic acid is hydrolysed to silica and calcium fluoride. These precipitates settle along with gypsum and rock dust in the settling basin. The clear overflow is either directly disposed to water course or subjected to secondary lime treatment for further removal of fluoride and phosphate.

When ammonium phosphate is the fertilizer material, the effluent from the plant consists generally of ammonium phosphate and ammonia. The phosphates are precipitated by lime treatment and the clear ammoniacal overflow may be further treated by some methods suitable for nitrogenous effluents. Apart from the above overflow may be further treated by some methods suitable for nitrogenous effluents. Apart from the above principal streams, a phosphate fertilizer works gives up a huge amount of uncontaminated cooling water. Present day practice is towards recovery of gypsum, rock dust and fluoride from these effluents.

Corrosion in Fertilizer Industry and Materials of Construction

Corrosion is a national problem. It is costing this country about Rs. 150-200 crores annually. The importance of a scientific approach to minimize its ravages has now been recognized. In the western countries national bodies, such as the National Association of Corrosion Engineers in USA, have been sponsored and maintained by the industries to carry out long range investigations in all aspects of corrosion problems. In India too, the Corrosion Advisory Bureau of the Metals Research Committee (CSIR), since its establishment 6 years ago, has been striving hard to focus the attention of the metal manufacturing and consuming industries on the need taking effective measures against corrosion. To its credit, the Bureau has already drawn the corrosion map of India and is now going to embark on their programme to collect systematic data on the rate of sub-soil and underground corrosion in the country.

The fertilizer industry encounters this problem in every phase of its operations. Because of the immense scale on which various operations are carried out and of the importance to minimize the shut-down periods, the corrosion problem in this industry must be viewed with seriousness. With this idea in view the Bureau

organized a short course in collaboration with FACT Technical Society on Corrosion in Fertilizer and Petroleum Industry at Udyogamandal (Kerala) during December 20-24, 1969. Later, in collaboration with the Indian Chemical Manufacturers' Association, it organized a seminar on corrosion in chemical industry at Bombay during Feb. 3-6, 1970.

In a paper, entitled 'Corrosion by Cooling Waters', presented at the above seminar, Sarbasri A. K. Roy and K. M. Verma of P & D Division, FCI Ltd. reviewed the factors that affect the rate of corrosion and fouling of cooling water systems including biological attack and have described the major variables, which are common to all systems and use of common methods to reduce corrosion including newer constructional material, case histories and hardware failures. The most widely used cooling water treatments in use today are composed of charomates, phosphates, zinc and the use of various synergistic materials of organic and inorganic nature. These materials can be used in any number of blends and combinations, the use of which is dictated by the type of operation, water circulation and the type of equipment. No particular substance can be applied widely to handle all situations.

Uniform attack is likely to be encountered in waters with a high content of dissolved salt and heterogeneity giving rise to pitting is a common mode of intense localized attack on materials of construction. Impingement attack is another form of erosion-corrosion, which specially occurs, when a turbulent aerated water-stream impinges against a metal surface and is associated with continuous local breakdown and removal of the protective film. Cavitation erosion may also occur when a liquid in contact with a metal surface is subjected to alternating changes in pressure; it can be divided into three types, viz. (i) one causing deformation and metal hardening of the metal, (ii) when less severe there would be fatigue cracking, and (iii) when the mechanical effects are still less severe corrosion in the most important factor and the attack would be of impingement type.

The different variables which affect the rate of corrosion and fouling are velocity, viscosity, dissolved solids, temperature, pH, micro-organisms, such as sulphate-reducing bacteria, iron bacteria, nitrosifying and nitrifying bacteria.

(i) *Effect of Velocity*: The diffusion rates of oxygen and cations to the metal surface are increased with velocity but with very high velocity the corrosion rate diminishes due to oxygen polarization of the cathodic areas which accounts for serious pitting of the tube ends in the water boxes.

(ii) *Effect of Viscosity*: By increasing the viscosity of the cooling system the diffusion coefficient of the ions at the interface is decreased, which in turn reduces the corrosion rate. The action of certain colloidal silicates for reducing corrosion is to increase viscosity.

(iii) *Effect of Dissolved Solids*: The effect of increasing the dissolved solids is two-fold, viz. increasing slightly the diffusion coefficients of the ions in dilute solutions and the solubility of low soluble compounds, e.g. calcium carbonate and phosphate.

(iv) *Effect of Temperature*: The overall effect is very complex and the following factors are affected: (a) diffusion coefficient is increased; (b) Solubility of various compounds and chemical reaction rate are increased.

(v) *Effect of pH*: pH changes the solubility of all the low-solubility compounds and affects the corrosion rate since as the pH is lowered the need for oxygen as cathodic depolarizer decreases and hydrogen can be discharged directly. Control of pH and dissolved solids reduce the rate of corrosion by water without addition of further chemicals in the system.

(vi) *Effect of Micro-organisms*: Microbiological fouling on metal surfaces (a) restricts flow and serves as a binder for suspended matter, (b) prevents the absorption of anodic inhibitor and (x) affords the oxygen-barrier necessary for the formation of colonies of anaerobic micro-organism underneath it next to the metal surface. The sulphate-reducing bacteria are the most important anaerobic microorganism in water systems. Another important microorganisms is iron bacteria which requires aerobic conditions.

In the treatment of the open recirculating system its cost versus the cost of repairs and downtime is an important factor in the choice of the measures to be adopted. In the treatment of cooling waters, there are broadly 4 major objectives, viz. preventing (a) scale formation on cooling surface (b) corrosion of the metals in contact with cooling water (c) fouling of cooling surfaces and (d) deterioration of the wood.

In a paper* read at a Symposium on Industrial Application of Stainless Steel at Durgapur during Nov. 21-22, 1969 sponsored by the Alloy Steel Plant (H.S. Ltd.), Durgapur and the All-India Stainless Steel Manufacturers' Association, Sarbsari K. M. Verma and A. K. Roy of P & D Division, presented case histories of failures of stainless steel equipment, including some studies on typical trouble-shooting to illustrate the complexity of such applications.

*Stainless Steel in Fertilizer Industry.

The wide variety of chemically aggressive media handled and the varied conditions under which processing is effected in the fertilizer industry play a crucial part in the selection of materials of construction in the different parts of plants. It may become necessary to vary the choice of type of alloy steel used from point to point in an equipment train. Table 1 gives a general idea of the extent of use of alloy steel in a typical fertilizer plant component unit. For convenience the data have been segregated for the following categories of steel finished: (a) Flat sections—plates and rounds for fabrication of vessels, for lining mild steel shells, for shaping into components of some moving machinery, (b) pipes (c) billets or ingots for fabricating forged pieces, for casting components for valves and pipe fittings or moving machinery, etc.

Though the data (Table 1) on typical requirements in

different types of alloy steel give the normal choices of varieties as currently preferred, the reliability of their performance in actual operations depends on the case with which the preliminary analysis of requirements for each situation is made, the case with which fabrication is done and the maintenance of correct conditions of operations in the plant environs. Numerous cases are there where even with utmost care failures in actual application have occurred due to factors which may have been initially overlooked or whose existence was not suspected.

Electrolytic Hydrogen Feedstock: Though most of the components of an electrolyser are made up of mild steel, certain parts which undergo frequent replacements due to corrosion have sometimes been changed to stainless steel. In the Nangal unit of FCI Ltd., the strips for holding the double diaphragms were changed to 18-8

TABLE 1—USAGE PATTERN AND FINISH

Plant Unit	Capacity	Type of S.S.	Flat thickness range, mm.	Te	Pipe size range mm.	Te	Billets, te.
Ammonia (Naphtha-based)	600 (1 stream)	AISI 304	2 to 3	4.7	20	8.1	4.5
		321	3 to 55	111.2	20 to 230	56.7	4.5
		347	—	—	20	0.2	—
		310S	—	—	30	3.4	—
		410	10	2.7	—	—	—
		Incolloy	—	—	—	—	—
		800	16	0.5	33 to 260	7.5	—
Urea	1000 (2 streams)	HK40	—	—	148	120	—
		316 ELC	0.82 to 60	243	10 to 800	101.5	54
Ammonia Sulphate (by Acid Neutralisation)	300 (neutralisers)	316 ELC	1 to 25	76.8	10 to 200	11.3	7
Ammonia Sulphate (Gypsum process)	1100 (3 streams)	AISI 321	1 to 25	24	25 to 200	6.5	2.5
		316	1 to 25	144.5	25 to 200	32	9.5
Nitric Acid	860 (2 streams)	310	5 to 15	22	25 to	3	—
		347	3 to 32	734	10 to 300	274	N.E.
Nitrophosphat	2000 (4 streams)	316	2 to 8	200	10 to 300	51	N.E.
Phosphoric	35 (as P ₂ O ₅) (single stream)	HV 3*	3 to 12.5	6	80 to 200	1.3	0.5
		HV 9*	1.5 to 12.5	25	80 to 200	3.0	3.5

*HV 9 contains Cr. 19 to 22% Ni. 24 to 26% Mo. 4 to 5%
 HV 3 contains Cr. 17% Ni. 12% Mo. 3%
 N.E. Not estimated

stainless steel but after a certain period of use some of the strips developed cracks. Investigations revealed that the material was of austenitic type with presence of slip bands. Metallographic examination revealed numerous intragranular cracks irrespective of the cell position. The failure is due to the conjoint action of 25 per cent potassium hydroxide at 80°C and stresses in the metal.

Air Liquefaction Plant: During pneumatic testing in the air liquefaction plant in the Trombay unit of FCI Ltd., leaks in the stainless steel vessels were detected in the different sections, the material of construction was 304 stainless steel. Most of the leaks were detected in the vicinity of welds, viz. within 2 inches.

Detailed investigations were carried out on a high pressure column which had five double welding seams with backing rings and seven single seam weldings. An inspection of the inside surface of the vessel, showed extensive bluish white deposits, which on analysis was found to be a mixture of copper chloride and free copper with 16 per cent of chloride, on the copper sieve plates which were fitted to the cylindrical column. Metallographic examination of the damaged and undamaged portions showed that the weld metal had dendritic structure with interdendritic segregation of carbide. The austenitic grains appeared plastically

strained. The cracking pattern was highly branched and was transgranular in nature. These observations showed that welding was of such a nature that post-welding heat treatment was necessary. The interdendritic segregation of carbide could have been caused by a high heat input during welding thin sheets on comparatively thick baking rings, subsequent slow cooling rate having activated the precipitation of carbide. The entire area in the vicinity of the weld had become plastically strained by thermal stresses.

Another case of corrosion of stainless steel vessels was observed in the air separator and nitrogen wash units. Some vessels in the plant after running for a few months showed the following types of corrosion: (i) general pitting distributed at random in most of the vessels but sometimes concentrated in localized zone with or without the deposit of brown rust; the trouble was traced to the presence of high chloride in the insulating material and stress; (ii) leakages at many points close to the weld seams.

The authors later dealt with the corrosion of stainless steel in some other plants manufacturing ammonium sulphate, nitric acid, ammonium nitrate, sulphuric acid and phosphoric acids, etc.

EDITOR'S NOTE

TECHNOLOGY accepts research papers from scientists and technologists outside FCI Ltd., provided these are:

- (i) original and related to science and technology
- (ii) approved by external referees chosen by the Editor, and
- (iii) communicated from reputed institutions and written by workers with adequate experience.

Papers for publication in TECHNOLOGY are, therefore, welcome. These should be sent in duplicate (complete with illustrations and abstracts) to the Editor. Short communications, research notes, etc. are also accepted. Books, reports, proceedings of symposia, conferences, etc., meant for review in this journal, are welcome.

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Lecture & Book Reviews

Technoeconomics of Phosphoric acid Production

Mr. M. D. Vijayaraghavan, Director of Projects, Dorr-Oliver (India) Ltd., Bombay, read before the Fertilizer Institute (FAI) in Delhi on the 4th October, 1969 a paper* on the technoeconomics of phosphoric acid production in India. Water solubility is still one of the most desired criteria of phosphatic fertilizer which is also more effective when granulated than when used as a powder or run-of-pile material. The production of high analysis granular plant nutrients means that phosphoric acid as an intermediate has to be used.

In the Indian context, phosphoric acid can be produced by the wet process using imported rock, by the conversion of imported elemental phosphorus into thermal phosphoric acid and by electrothermal phosphorus and thermal phosphoric acid from imported phosphate rock and using cheap power. In all cases, indigenous rock phosphate discovered in Rajasthan could also be used.

According to the information available, the imported phosphoric acid at present costs Rs. 1000 per ton of P_2O_5 at 54 per cent P_2O_5 phosphoric acid CIF Indian port. To this, if cost of storage, handling and import duty at $27\frac{1}{2}$ per cent is added, the total cost works out to Rs. 1,315 per ton of P_2O_5 , as compared with locally produced acid of Rs. 1,270 per ton of P_2O_5 in a phosphoric acid plant of 200 tonnes/day of P_2O_5 capacity. As regards the foreign exchange expenditure, as imported acid, Rs. 1,000 per ton of P_2O_5 would be needed, whereas for production of phosphoric acid in India, 3.5 tons of rock phosphate and about 1 ton of sulphur work out to about Rs. 970 per ton CIF which leads to a saving of about Rs. 30 per ton of P_2O_5 as saving of foreign exchange. This is relatively a minor saving at the present level.

The estimated cost of production of thermal phosphoric acid on the basis of

Proceeding No.6, The Fertilizer Institute, (The Fertilizer Assn. of India, New Delhi)

imported rock phosphate and power at the rate of 2.5 paise per Kwh works out to about Rs. 1,320 per tonne of P_2O_5 of 54 per cent strength of phosphoric acid produced in a plant capacity of 200 tonnes/day P_2O_5 located in a port. Though this is costlier by about Rs. 50 per tonne of P_2O_5 than by wet process phosphoric acid production there is an outstanding advantage in the saving of foreign exchange of Rs. 340 per tonne due to avoiding of the import of sulphur.

The investment per ton of P_2O_5 is higher in the cost of electrothermal phosphoric acid as against wet process acid by about 40 per cent. The import content of the plant would also be higher for the electrothermal phosphorus plant as against the wet process plant. Where bulk electric power is available at relatively lower cost elemental phosphorus could be produced. The total cost of conversion of P_4 to P_2O_5 expressed per tonne of P_2O_5 including its storage and handling in a plant located in an Indian port will be about Rs. 100. If we assume that the cost of production of P_4 in U.S.A. would be similar to that of wet process acid and assuming a freight rate of \$. 30 per tonne of phosphorus, then the cost of phosphoric acid produced in India from imported elemental phosphorus works out to about Rs. 940 per tonne of P_2O_5 for the import of phosphoric acid. This represents a saving of about Rs. 100 per tonne of P_2O_5 which is substantial. The cost of elemental phosphorus may reduce further in the coming year with the possibility of low cost nuclear power in U.S.A. in which case the import of elemental phosphorus instead phosphoric acid may be more attractive. Wherever low cost phosphate rock and low cost power are available, the cost of phosphorus should prove more attractive as a fertilizer intermediate than phosphoric acid, due to the considerable freight advantage.

Most of the plants in India would still be based on the conventional wet process and a modification of the same, namely hemihydrate process.

The detailed study of the following should prove worthwhile: (1) Study the

relative economics of import of phosphorus or phosphoric acid in India compared with local production. Preliminary review shows that local production is the ultimate answer. (2) Study the technoeconomic feasibility of production of phosphoric acid or elemental phosphorus in Rajasthan or elsewhere, based on indigenous raw materials. (3) Study the economics of production of elemental phosphorus and its transportation to other phosphatic fertilizer plants located at the coast or inland. (4) Emerging from the above, recommendations could be made by an expert body to the Planning Commission on targets, capacities and locations for elemental phosphorus and phosphoric acid during the Fourth Five Year Plan, in order to bridge the gap between the estimated capacities and the targets for P_2O_5 fixed for 1973-74.

An Application of Transportation Model to Fertilizer Industry in India [D. K. Desai and S. B. Tambad, Indian Institute of Management, Ahmedabad, 1969]

Transportation of fertilizers for their distribution and use from the supply and manufacturing centres to various parts of the country constitutes a substantial portion of the consumer price. 9.6 lakh tonnes of fertilizers were consumed in India in 1966-67 which is expected to rise to 3.55 million tonnes by 1974-75. India is also expected to be self-sufficient in the use of fertilizers. However, efforts should be made to reduce the cost of production of fertilizers which is very high and also the best type of planning should be made to reduce the cost of marketing and transportation so that ultimately the poor and common farmers of our country get considerable relief in purchasing the fertilizers in time.

D. K. Desai and S. B. Tambad have studied whether it is possible to minimize transportation cost of fertilizers from the points of view of both consumers and producers by using the transportation model which is a particular type of linear programming. To solve the problems of transportation of fertilizers, this technique

has been converted to a simplex model which can be used to solve any linear programming problem. After the data were fitted into the simplex model the solutions were obtained by running the models on the IMB computer 1620. As more than three-fourths of fertilizers in the country are transported by rail, the study was confined within the rail transportation cost. Transportation models have been used to give the optimum programme of distribution of fertilizers. Minimum transport cost arrived at by this method has been compared with the actual cost for the year 1963-64 and then the minimum cost for the projected production and consumption of fertilizers for 1974-75 has been tried to be determined.

The following objectives were set for the study: (1) To determine the minimum transportation cost of fertilizers from the ports or production centres to the consuming centres. (2) To compare the transportation costs of fertilizers arrived at by the use of the transportation model with the "actual costs" and to determine the extent of savings that could be achieved by following the transportation cost minimization programme. (3) To discuss the policy implications on pricing of fertilizers and locational advantages of fertilizer factories based on the results of analysis.

No *a priori* judgement was taken that a particular route of transport from production centres and ports to the consumption centres would have the best route.

For the year 1963-64 the supplies and demands were considered in terms of the physical quantities of fertilizers for urea and other fertilizers (sulphate of ammonia, calcium ammonium nitrate, etc.) and for 1974-75 they were considered in terms of nitrogen.

The results of analysis of the data for 1963-64 indicate that on the whole there was a net saving of Rs. 2.069 lakhs or 3.64 per cent in the transportation cost of urea and Rs. 37.934 lakhs or 9.51 per cent in the transportation cost of other fertilizers by the use of the optimum programmes as compared to the present programmes. The total savings in cost of transportation with respect to both urea and other fertilizers work out to Rs. 40.003 lakhs or 7.92 per cent of the cost of the present programme. Several changes in the quantities to be transported and also the origins from which they have to be transported to the different destinations have been indicated by the optimum programmes in comparison to the present programmes. The

total transportation cost for 3,88,896 tonnes of nitrogen from the producing centres and ports to consuming centres in 1963-64 was 4,15,77,000 rupees. The average transport cost per tonne was 106.91 rupees.

A maximum saving of Rs. 17.069 lakhs was obtained for the South-zone which was followed by a net saving of Rs. 12.653 lakhs in the North-zone. It is interesting to note that in the case of the Western-zone there were no savings in the costs of transportation of urea indicating that the present programme was optimum. However, a saving of Rs. 9.48 lakhs in the case of other fertilizers was obtained in the Western-zone. There was a saving of Rs. 0.792 lakhs in North-eastern zone.

The shadow prices obtained for the production centres or ports and the consumption centres have considerable importance for formulating policy decisions. The shadow price of the origin (production centres and ports) indicates the intrinsic value for the locational advantage of the fertilizer factories or ports of one additional tonne of fertilizer if it was produced and transported to any of the destinations. The shadow prices of the destinations denote the value added to one tonne of fertilizer after it was transported to the destination from any origin.

The shadow prices for the transportation of urea in the Western-zone indicated that Madras had the best locational advantage for a new fertilizer plant or increasing existing production for supplying at the same price to any of the States in the Western-zone, the cost of production having no bearing on location. With the cost of production remaining the same at all origins it would be most desirable to step up consumption in Maharashtra followed by Gujarat, Mysore, Goa and M. P respectively. In the North-zone the shadow prices have indicated that it would be desirable to step up production at Sindri followed by imports at Calcutta if the cost of production were to remain the same. In the North-eastern zone, it would be advantageous to import urea from Calcutta than produce at Sindri if the cost of production at Sindri and the import price at Calcutta were the same. In the South-zone, Madras enjoyed the best locational advantage. If the price is to remain the same at all the destinations, then the cost of production has to be lowered by Rs. 14.2 at Bombay and Rs. 12.9 at Vizagapatam than that at Madras.

In the Western-zone, the shadow prices for the transportation of other fertilizers indicate that Bombay would enjoy the best locational advantage. In the North-zone the best locational advantage was with Sindri. In case of the Eastern-zone the price of a tonne of fertilizer could be higher by Rs. 26.2 at Assam, Rs. 6.2 in Orissa, Rs. 31.3 in Manipur than that in West Bengal if the cost of production was the same at different plants and the plants were to bear the transport cost. If the price has to remain the same at all the destinations then the costs of production could be higher to the extent of Rs. 33.7 at Calcutta, Rs. 17.0 at Sindri, Rs. 18.4 at Tata Iron (Jamshedpur), Rs. 20.8 at Indian Iron (Burnpur-Asansol), Rs. 16.8 at Barrakur, Rs. 6.8 at Bhilai and Rs. 13.6 at Rourkela than that at Nangal. In the Southern-zone, the shadow prices indicate that Madras enjoys the best locational advantage. In case of Western and Southern-zones it was better to import than to expand production at various plants if the cost of production at the various production centres and the import price at the ports were the same. For imports it was better to use Bombay for the requirements of Western-zone, Madras for Southern-zone and Calcutta for North-eastern and Northern zones.

The State-wise requirements and the factory-wise production of nitrogen for the year 1974-75 were collected. The freight rates to transport a tonne of nitrogen from the various origins to the different destinations were calculated. For this purpose a composite freight rate was arrived at by taking into consideration the amount of nitrogen obtained through urea, diammonium phosphate and other fertilizers and by adopting the respective weightage.

As the size of the problem was large and it could not be run on the IBM Computer 1620, the country was divided into two zones. The quantity to be transported from various origins to the different destinations according to the optimum programme for the North and South zones are given in Tables 5.1 and 5.2 respectively. The total quantity of nitrogenous fertilizers in nutrient terms which was estimated to be transported during 1974-75 from various production centres and ports to consuming centres was 36,45,320 tonnes. The total cost of transport according to the optimum programme was Rs. 23,61,47,000 giving an average transport cost of Rs. 64.78 per tonne.

Assuming that the cost of production of

fertilizers is the same at all production centres, the optimum programme in the North zone, shows that Punjab should get its supplies from Kandla, Kotah, Delhi, Baroda and Namrup. Haryana should get its supplies from Kandla and Okha. Rajasthan should obtain its supplies from Kanpur, Mirzapur, Gorakhpur, Sindri, Namrup and Varanasi. Madhya Pradesh should get its supplies from Baroda only. Bihar is to obtain its supplies from Sindri, Gorakhpur and Barauni. Orissa should derive its supplies from Rourkela and Durgapur. Assam should get its supplies from Durgapur and a small quantity would be required to be imported.

In the South zone, according to the optimum programme, Maharashtra should get its supplies from Bombay only. Andhra Pradesh should derive its supplies from Goa, Neyveli and Alwaye. Madras should get its supplies from Madras, Neyveli and Alwaye. Kerala should obtain its supplies from Cochin only. The excess supplies in Goa and Mangalore perhaps would be required to be exported.

The shadow prices of the origins and destinations for the North and South zones, are given in Tables 5.5 and 5.6 respectively.

In the North zone, the shadow prices of the origins are Rs. 195.70 from Nangal, Rs. 72.80 from Okha, Rs. 137.50 from Kotah, Rs. 191.10 from Delhi, Rs. 152.70 from Kanpur, Rs. 142.20 from Mirzapur, Rs. 151.90 from Gorakhpur, Rs. 134.30 from Baroda, Rs. 100.40 from Sindri, Rs. 76.30 from Rourkela, Rs. 90.20 from Durgapur, Rs. 120.80 from Barauni, Rs. 148.80 from Varanasi as compared to that from Namrup. This indicates that from the point of view of transportation cost, it would be desirable to step up production at Nangal, Delhi, Kanpur, Gorakhpur and Varanasi in order of preference as compared to other origins.

The shadow prices for the destinations indicate that additional values amounting to Rs. 247.80 at Punjab and Haryana, Rs. 210.70 at U.P. Rs. 191.00 at Rajasthan, Rs. 159.10 at Gujarat, Rs. 219.80 at M.P., Rs. 89.60 at Assam, Rs. 161.10 at Bihar, Rs. 178.70 at Orissa and Rs. 132.60 at West Bengal if fertilizers with the same production cost were transported to these destinations. The differences in the shadow prices among the destinations indicate the price differentials likely to prevail among the different destinations under conditions of perfect competition. If the free market conditions are to prevail and there would

be no government or other regulations, the prices per tonne are likely to be higher by Rs. 158.20 in Punjab and Haryana, Rs. 121.10 at U.P., Rs. 101.40 at Rajasthan, Rs. 69.50 at Gujarat, Rs. 130.20 at M.P., Rs. 71.50 at Bihar, Rs. 86.10 at Orissa and Rs. 43.00 at West Bengal than those at Assam during 1974-75. It is assumed that the cost of production would remain the same at all factories and for imported fertilizers.

In the South-zone (Table 5.6) the shadow prices of the origins are Rs. 4.70 at Bombay, Rs. 9.30 at Vishakhapatnam, Rs. 76.00 at Madras, Rs. 22.20 at Neyveli, Rs. 19.60 at Alwaye, Rs. 3.20 at Cochin, and Rs. 55.80 at Ennore as compared to those at Goa and Namrup. If the production is to be stepped up it would be most desirable to increase it at Madras and Ennore from the point of view of transportation cost. The shadow prices of the destinations indicate that the values added per tonne of nitrogen are Rs. 5.10 in Maharashtra, Rs. 122.90 in A.P., Rs. 105.90 at Mysore, Rs. 76.40 in Madras, Rs. 56.70 in Kerala. The differences in the shadow prices of the destinations reveal that the prices are likely to be higher by Rs. 117.80 in Andhra Pradesh, Rs. 100.80 in Mysore, Rs. 71.30 at Madras, Rs. 51.60 in Kerala than that in Maharashtra.

The models provide information on shadow prices which can act as guides for policy makers in framing suitable policies. The results according to optimum programmes and the shadow prices in the transportation models have been given in Tables.

The operational research study by the authors and results found should be a valuable guide to the producers of fertilizers as to the areas which would prove more profitable to them and where they should increase or reduce their sales efforts. The results should also provide guidelines to the policy makers of the country to arrive at more pragmatic policies in the distribution of fertilizers. The use of these techniques would be valuable to the manufacturing units to work out their sales strategies, determine the location of warehouses and solve a host of other problems.

The study has been made only on the transportation of fertilizers by rail from one railway station to another. Distribution of fertilizers to the farmers from the nearest railway station is also very important. While transportation cost minimization of fertilizers is no doubt an important factor,

top priority must be given that fertilizers reach to the farmers at the time of their need.

[Benoy K. Banerjee]

Corrosion in Chemical Industry: Edited by K. N. Rao & A. K. Lahiri, Price Rs. 20.00 (Published by Indian Chemical Manufacturers' Association, Bombay Regional office, Sir Vithaldas Chambers, 16, Apollo Street, Bombay-1, BR).

The book contains the proceedings of a seminar jointly organized by the Corrosion Advisory Bureau of the Metals Committee of the Council of Scientific and Industrial Research and the Indian Chemical Manufacturers' Association held in Bombay in February, 1969. It deals with various aspects of corrosion problems in the chemical industry and will prove useful to the persons concerned. The different articles presented by specialists in the field in India have been dealt with both from practical and theoretical considerations.

In the introductory paper, entitled 'Problems of Corrosion and its Prevention with Specific Reference to Chemical Industry', D. M. Trivedi of ICMA has dealt with the role of corrosion prevention in the conservation of critical raw materials in the light of the technological developments in the chemical industry. In this connection, he has discussed the possibilities of use of plastics, synthetic rubber, high temperature structural plastics, sprayed metallic coatings, special corrosion-resistant materials, including special type of stainless steel and titanium, aluminium, epoxy coatings, isothalic polyester resins, and reinforced plastics in chemical industries and their limitations. He has then dealt with the corrosion case histories in some of the chemical plants and remedial measures taken.

Another paper presented was on 'Corrosion in Caustic Soda Industry: Some Case Histories' by S. R. Addanki, K. P. Mukerji and A. K. Lahiri from National Metallurgical Laboratory, which dealt with the corrosion of mild steel in saturated brine solution and corrosion of nickel in steam condensate containing air and carbon dioxide. The results of laboratory experiments under simulated conditions on the corrosion of nickel are also presented. This paper also deals with the corrosion of cast iron pots used for fusing caustic soda. Some of the other papers presented were 'Corrosion of Steel by Formaldehyde' by S. K. Chakravarty, S. K. Sanyal, S. N. Pandey, and B. Sanyal from Defence Research Laboratory (Materials) and 'Role of

Some Physico Metallurgical Factors on Stress-corrosion Cracking' by A. K. Lahiri and T. Banerji from National Metallurgical Laboratory.

N. M. Lotlikar of NOCIL in his paper 'Chemical Complexes and a Corrosion Engineer' has emphasized the need for a corrosion engineer in every chemical plant. In his paper, 'A Case Study in Dehydration of Hydrochloric Acid,' S. S. Vengsarkar dealt with the severe corrosion problems coupled with poor mechanical design that led to the abandonment of the facilities. In the paper entitled Case History of Corrosion Failures of Some Equipments and their Preventive Measures, S. K. Sanyal and B. Sanyal from D. R. L. (Materials), have dealt with case histories of corrosion failures of some equipment by formaldehyde, caustic soda and detergent liquids. W. A. Wahbe and J. S. R. Krishna Rao from Regional Research Laboratory, Hyderabad have given a brief history of the development of glasslined equipments in their paper on 'Protective Coating for Chemical Service'. P. R. Mehta, M. J. Mehta and K. Seshadri from Central Salt and Marine Chemical Research Institute have described some corrosion problems met with in handling salt waters in their paper, entitled 'Study of Corrosion in Salt Waters'.

A paper on 'Corrosion by Cooling Waters' was presented by A. K. Roy and K. M. Verma of Planning & Development Division, Fertilizer Corporation of India Ltd. It deals in details with the various theoretical aspects of the problems encountered in the handling of cooling waters such as forms of attack, the different variables affecting corrosion, viz. effect of velocity, viscosity, dissolved salts, temperature, pH and micro-organisms. It also deals with the different aspects of cooling water treatment, viz. prevention of scale formation, corrosion, and fouling and lastly the prevention of deterioration of wood as also the various measures being taken for their control were also discussed. For the prevention of corrosion, the measures being taken, such as corrosion control by control of pH, by use of inhibitors and cathodic protection, were discussed. The use of common inhibitors, like nitrite, silicate, benzoate, chromate, and polyphosphate, and different inhibitors based on chromate and polyphosphate was described and a large number of case histories have been cited from the authors' own experience in the fertilizer plants and also from the literature. Pre-treatment of cooling water and mention

about the proper selection of materials for the cooling tower service has been made. In his paper on the 'Operating Experience of a Large Cooling Water System in the Chemical Plant', C. R. P. Sharma from Synthetics and Chemicals, Bareilly, described the difficulties experienced during the operation of their factory cooling tower. H. V. Kunikullaya and D. M. Srinivasan from Golden Chemicals have found chromate to be an effective inhibitor for most metals and alloys.

On the use of non-ferrous metals in chemical industry, B. K. Murty from Indian Aluminium Co and N. Srinivasan from Indian Lead-Zinc Information Centre presented papers, wherein the application of these two metals and their alloys, in different chemical environments, was discussed.

K. N. P. Rao of Metals Committee, CSIR, highlighted some of the developments that have taken place in the evolution of new types of steel to meet the needs of chemical industry. In his paper K. P. Mukherji from National Metallurgical Laboratory discussed design aspects to control corrosion of process equipments.

On the use of protective coatings two papers were presented, viz. (i) 'The Protective Action of Paints, Varnishes and Lacquers' by K. S. Rajagopalan and S. Guruviah from Central Electro-Chemical Research Institute, and (ii) 'Modified Primer for Industrial Structures' by V. B. Soni of Dharamsi Morarji Chemical Co. The first paper dealt with the mechanism of protection afforded by the coatings in relation to different types of pigments and other ingredients of the paint.

In 'Measurement and Evaluation of Corrosion Damage', B. Sanyal and S. K. Gupta of Defence Research Laboratory listed the different types of attack and methods used to evaluate damage. Lastly, K. S. Rajagopalan of CECRI Karaikudi discussed the need for detailed knowledge about the metal and environmental factors for an adequate assessment of the problems.

The printing is fairly good. Unfortunately, page numbering has not been done properly—after page 60 the pages are not numbered. Such an important and useful publication should have carried a 'Contents' page. There are printing errors also.

[S. N. R.]

Corrosion in Fertilizer and Petroleum Industry edited by K. N. P. Rao and A. K. Lahiri, 159 pages, Price Rs. 25.00 (Obtain-

able from Publications and Information Directorate, CSIR, New Delhi-12)

It contains the proceedings of a short course on Corrosion in Fertilizer and Petroleum Industry arranged and organized by the Corrosion Advisory Bureau of the Metals Committee, Council of Scientific and Industrial Research, at Udyogmandal (Alwaye) in December 1968. The Corrosion Advisory Bureau has done a very useful service for the workers connected with corrosion research and plant maintenance as it deals with varied types of corrosion problems met in the fertilizer and petroleum industries.

The book starts with an introduction by Sir J. J. Ghandy, Director, TISCO, who is the chairman of the Metal Research Committee. He has laid stress on the problems facing the fertilizer and petroleum industries emphasizing the need for a coordinated approach. In the Introductory lecture Sri A. K. Roy, Superintendent, Chemical Research Wing of the Planning & Development Division, Fertilizer Corp. of India, has dealt with the varied types of corrosion problems met within the fertilizer and petroleum industries and areas where research is essential. He has mentioned the use of the different corrosion-resistant materials, coatings, inhibitors, non-metallics, anodic and cathodic protection and design aspects in the control of corrosion problems. The different articles presented by specialists in the field in the country have been dealt both from the practical and theoretical aspects and have been divided into five different groups sessionwise.

Session I: The following 2 papers are grouped in this session: (i) Chemical Corrosion and its Prevention by N. Subramanyam of Central Electrochemical Research Institute, and (ii) Intergranular and Stress-Corrosion Cracking by A. K. Lahiri of National Metallurgical Laboratory. The former deals with different types of corrosion attack and the general methods of its prevention which are in use, while the second deals with the factors responsible for intergranular attack and methods of prevention, the different alloys and the conditions under which they undergo stress-corrosion cracking and the remedial measures.

Session II: Under this session the first paper by A. K. Roy and K. M. Verma of the P & D Division (FCI) deals in detail the various types of corrosion problems encountered in the manufacture of different nitrogenous fertilizers, sulphuric acid, phosphoric acid and superphosphate. Starting

with the different hydrogen sources viz. electrolytic processes, coke oven, refinery gas and natural gases, naphtha, etc., the different types of corrosion problems encountered in the stepwise processing of the gas till the end-product is obtained have been mentioned. A large number of case histories have been described, some from the authors' own experiences and others from the literature. Corrosion problems in plants, viz. reformation, synthesis gas purification, ammonia synthesis and storage, ammonium sulphate, ammonium nitrate, nitric acid, nitrolimestone and ammonium chloride plants have been described. The corrosion problems encountered in the manufacture of sulphuric and phosphoric acids and superphosphate have also been described with numerous case histories.

Session III: Under this session, dealing with the corrosion problems in the petroleum industry, 2 papers, viz. (i) Corrosion Problems in the Petroleum Industry by A. K. Lahiri and H. R. Thilakan from NML and (iii) Corrosion and Erosion problems in the Petroleum Refineries by G. Rama Rao of Indian Oil Corpr., were presented. The first paper deals with the

corrosion problems in the production equipments, such as internal wall corrosion corrosion of pumps, valves, etc., and their control by inhibitors. The external corrosion of wall casing has also been described. The problems connected with the corrosion of crude treatment equipments, such as storage tanks and refining equipments, and those in the reformer and desulphurization units and its prevention has been described. The second paper deals with the corrosion and erosion problems in the petroleum refineries, and the various factors which cause them. Some important case studies of plant failures are also described along with their preventive measures.

Session IV: In this session, R. K. Banerji and C.P. De of Naval Chemical and Metallurgical Laboratory, Bombay have dealt with the external and internal corrosion of storage, underground tanks and pipelines and corrosion of tankers. Their paper also describes some of the corrosion problems in the phosphatic fertilizer and liquid nitrogen production and their remedial measures.

Session V: Under this session, there are

3 papers and a chapter on special corrosion problems. The first paper by K. S. Rajagopalan (CECRI), Karaikudi deals with the effect of water composition, presence of bacteria, effects of flow, temperature and heat transfer and the preventive measures for the inhibition of water-side corrosion. The next 2 papers, viz. (i) Cathodic Protection of Metals and (ii) Corrosion of Structural Metals, are by K. P. Mukherjee (NML, Jamshedpur). The first one deals with the principle of cathodic protection, anode material, back fill, economic aspect and field application. The second paper gives the comparative performances of different structural materials and the protective measures, such as painting and metallic coatings. It also described briefly the underground or underwater corrosion and the protective coatings used in petroleum production.

The printing as well as get-up are good and the discussions at end of each chapter are useful. However, each paper should have carried an abstract.

[S. N. R.]

Notes & News

Polyphosphate via Simplified Route

The new direct route, covered by a recent US patent (no. 3464808) developed by Swife Agricultural Corp., features direct reaction of anhydrous ammonia with orthophosphoric acid to produce solutions and suspensions of ammonium polyphosphates. Liquid anhydrous ammonia is fed to a vaporizer where it contacts (via a double-pipe heat exchanger) recirculated fertilizer product. The ammonia gains heat and is vaporized while the product is being cooled. The gaseous ammonia then passes to a pipe reactor. There it is joined by orthophosphoric acid that has been preheated by travel through a steam heat exchanger. Both streams enter at 10-15 psig the reactor which is 12 ft. long, 4 in. diam., 10-gauge, type 316 stainless steel pipe.

In the pipe, ammonia and acid are held at a mole ratio of around 1.6/1.0. They exothermally react immediately upon contact with one another. The heat of reaction causes a rapid rise in the temperature within the reactor—vaporizing the free water in the phosphoric acid. Further heat evolution releases the chemical combined water—triggering the polymerization of orthophosphoric acid. A number of compounds of varying chain length are formed, most prominent among them being pyrophosphate and tripolyphosphates. The reaction temperature is allowed to increase to 560 to 600°F giving a conversion of greater than 60 per cent. At this level, polyphosphates with highest stability and solubility are produced. The residence time in the reactor is sought to prevent side reactions—the formation of insoluble types of phosphates—from occurring.

From the reactor there are two phases. Unreacted ammonia as well as steam generated in the reactor exist, as a gas. The ammonium polyphosphates leave as a molten liquid. The two phases empty into a mixing tank that holds liquid product at a level above that of the reactor exhaust. The tank liquid has a pH 6.2-6.4 controlled by the ratio of ammonia to phosphoric acid and a temperature of about 180°F, thanks to cooling in the ammonia vaporizer

and the action of a separate shell-and-tube cooler utilizing cooling water. The products emerging from the pipe are immediately quenched by the liquid and neutralized.

Potash can be added in the tank to provide K_2O value to the fertilizer, and when more than a saturation level of polyphosphate is produced, clay can also be added to maintain a suspension. Fertilizer is then stored in two separate vessels for 12-40-0 and 5-15-30 products respectively as well as a tank for nitrogen solution. By proper blending of these three, practically any liquid or suspension (nitrogen/phosphorus pentoxide/potassium monoxide) can be supplied.

[*Chem. Engng.*, 76 (27) (1969), 94]

Nuclear-based ammonia/desalination complexes

In recent years, interest has become widespread in the possible use of nuclear reactors as a source of inexpensive electric power and heat for industrial application, since these would make a number of processes attractive which may otherwise be uneconomic. Of special interest at the present time is the particular suitability of a combined desalination/ammonia synthesis complex based on the energy obtained in a nuclear power plant. The accent has been on the production of ammonia synthesis gas by electrolysis. In a paper presented at the Madrid symposium on nuclear desalination held in November 1968, a technique was described in which the heat evolved in a nuclear reactor, could be directly used to provide the reaction conditions for primary steam-reforming. The results of studies performed on the feasibility of an ammonia/desalted water complex, based on a natural gas-fired energy centre, on the application of a high temperature, gas-cooled nuclear reactor (HTGR) indicate that an ammonia/water facility is a reasonable economic proposition.

In a HTGR reactor designed to operate at 840 MW, the heat transfer between the

fuel elements of the reactor and the steam-generating coils is achieved by using a circulating stream of helium operating at between 760 and 1430°F and around 700 psia. Steam is generated at 2400 psia and 1000°F. At these elevated temperatures, it becomes practical to utilize directly the heat content of the helium transfer medium in order to provide the necessary energy for steam-reforming of natural gas or naphtha and in addition to generate the high pressure steam, required as feed stock in the reforming reaction together with the steam requirement for plant compressors and for a desalination operation. This system allows considerable flexibility between the amounts, desalted water, and electricity which are produced and has the advantage that only feed requirements of hydrocarbons are needed resulting in a saving of about one-third of natural gas or naphtha consumption compared with a conventional reforming operation. The advantages of this technique are obvious for locations in which hydrocarbon costs are high.

The temperatures and pressures at which reforming could take place would be only slightly less in the nuclear centre than in the conventional gas fired primary reforming furnace. Reaction conditions of 1400°F and 300 psia are envisaged and this would require only minor modifications to the steam/methane ratio. The system would require about 14 per cent of the reaction heat to support the reforming reaction together with another 6 per cent for the production of high pressure steam to supplement that produced in waste heat boilers to make up the total compressor drive requirement for the ammonia facility. The bulk of the high pressure steam which is produced in the nuclear centre is used to drive the vapour compressor turbines, producing desalted water, or alternatively to drive turbo-generators for the production of electric power.

The gases produced in the primary reforming operations out-lined above pass for further treatment to a basically conventional ammonia plant consisting of a

secondary reformer, the usual stages of carbon dioxide removal, shift conversion, methanation and finally synthesis conversion.

On the basis of the 840 MW nuclear generator being constructed at Fort Vrain, a complex consisting of ammonia production and water desalination units could produce 1500 stpd of ammonia and 179 gal/day of desalinated water. Both the

fixed and variable costs of operating the unclear facility are offset by transferring these to the costs of the ammonia and desalination operations. These are allocated 20 per cent to the ammonia plant and 80 per cent to the desalting plant on the basis a total of 20 per cent of the energy generated in the nuclear reactor is utilized for steam-reforming and for driving the ammonia plant compressors. In Table 1 the total

operating costs for the ammonia and desalination plants are given, based on two separate natural gas prices—a low price of \$ 0.15/mm Btu and a high price of \$ 0.40/mm Btu. With individual cost items assigned in a different manner to that in the above table, it is possible to produce a whole range of complementary costs which absorbs the expenses of the operation. In the above exercise, a nuclear-based complex appears quite viable when producing ammonia and desalted water above. It has been stated that the costs involved would be even more attractive for a complex which was expanded to include further production facilities such as phosphorus, diammonium phosphate, etc.

[Nitrogen No. 62, [(1969), 33]

TABLE 1—ANNUAL VARIABLE CHARGES AND COST OF PRODUCTION OF WATER AND AMMONIA

	Ammonia	Nuclear steam generation	Water desalting
Nominal rating	1,500 s.t.p.d.	840 MW (th)	179 million gal p.d.
Annual Raw Material and Energy Requirements			
Natural gas, 10 ¹² Btu	9.9	—	—
Nuclear fuel, 10 ¹² Btu	—	22.6	—
Electric power, 10 ⁶ kWh	19.6	14.0	—
Boiler feedwater, 10 ⁶ gal	269	75	—
Production cost (low gas price)			
Natural gas @ \$0.15/10 ⁶ Btu	\$1.48 million	—	—
Nuclear fuel @ \$0.15/10 ⁶ Btu(1)	—	\$3.4 million	—
Electric Power @ \$0.0045/kWh(2)	\$90,000	\$60,000	—
Boiler feedwater @ \$0.29/1,000 gal	\$80,000	\$20,000	—
Transfer costs of nuclear plant	\$700,000	(\$3.48 million)	\$2.78 million
Total variable costs	\$2.35 million	—	„
Total fixed charges (3)	\$5.24 „	—	\$13.35
Total annual charges	\$7.59 million	—	\$16.13 million
Cost of production			
—\$/s. ton ammonia	15.5	—	—
—\$/1,000 gal	—	—	0.27
Production cost (high gas price)			
Natural gas @ \$0.40/10 ⁶ Btu	\$3.96 million	—	—
Other variable costs, as detailed above	\$870,000	—	\$2.78 million
Total fixed charges (3)	\$5.24 million	—	\$13.35 million
Total annual charges	\$10.07 million	—	\$17.01 million
Cost of production			
—\$/s. ton ammonia	20.5	—	—
—\$/1,000 gal	—	—	0.27

(1) Based on equilibrium operation with U-233 recycle; uranium ore at \$8 per lb; separative work at \$26 per unit; and a 7% working capital charge. This cost is equivalent to \$0.0051 per kWh.

(2) Assuming electrical power generation from nuclear energy.

(3) Total fixed charges.

Cheaper Ammonia Feedstock in UK

ICI has signed a contract with the Gas Council on Aug. 18, 1969 covering long-term supply of 1000 therms annually of North Sea natural gas to ICI's complexes at a price which means that nutrient nitrogen will be produced considerably cheap. A comparison of prices paid by farmers, after deducting the Government subsidy, shows that whereas from the late 1950s to early 1960s prices paid by farmers for their fertilizers declined by upto 6 per cent by 1967/68 these had risen to the 1956/57 level. This rise was wholly due to the rising costs of imported raw materials which were only partially offset by improvements in manufacturing processes. Since early 1967 the following factors further increased fertilizer prices: closure of the Suez canal led to the imposition of a surcharge on petroleum raw materials, devaluation of pound sterling, small advances made in the nitrogen treatment of pastures, out break of foot and mouth disease of livestock, etc.

Although the UK has actively engaged in the largescale export of fertilizer nitrogen for a considerable period, this business has been largely restricted to ammonium sulphate only supplemented by small quantities of urea, CAN etc. ICI has commissioned in October 1966 an addition to its Billingham complex. Now, when the nitrogen export market is becoming increasing by competitive, UK is fortunate in being able to produce cheaper nitrogen from North Sea gas than from the current feedstock, viz. naphtha. The economic base will have its effect not only on the domestic fertilizer market but also on the world nitrogen export market. Nevertheless, as confirmed by several UK producers

the export market is regarded solely as a secondary outlet of course, domestic market will also depend on the extent to which UK farmers are prepared to accept high concentrations ammonium nitrate types, such as ICI's Nitram.

[*Nitrogen*, No. 62, (1969), 15]

Arabian Gulf—Nitrogen Supply

The vast oil and natural gas resources in the Arabian Gulf countries—Iraq, Iran, Kuwait, Qatar and Saudi Arabia—have prompted the area to develop rapidly to manufacture huge quantity of ammonia. Because of the negligible domestic demand of fertilizers in all these countries except Iran, an overwhelming proportion of the nitrogenous output will be exportable to the Asian continent and other parts of the developing world. By 1970, 700,000 tonnes of exportable nitrogen will be available from this region and by 1975 it is expected to rise to 1 million tonnes. Iran is the only country in this region where the usage of fertilizers has become popular among the farmers. The total N produced in this country during 1966-68 was 26.8 thousand tonnes and total consumption was 46.1 thousand tonnes. Domestic resources now supply only 50 per cent of the country's current level of usage. The Indian and Iranian Governments have come to an agreement with regard to joint participation in an ammonia project in Iran.

During 1967-68 Kuwait produced 50.5 thousand tonnes of N. Among the five Gulf nitrogen manufactures Kuwait has occupied the most prominent position. Kuwait Petrochemical Industries Co. (KPIC) has a large share in Morarji Kuwait Fertilizer Ltd. in India for which Kuwait is authorized to supply ammonia together with sulphur and phosphate rock.

The second largest nitrogenous outlet is Iraq. In Saudi Arabia and Qatar also several fertilizer plants are coming up.

By utilizing their waste natural gas in the manufacture of ammonia and nitrogen fertilizers largely for export, it is evident that the Gulf area will become a dominating force in the pattern of commercial transactions covering fertilizer nitrogen in the Indian Ocean area. Ammonia capacity planned for operation in the Arabian Gulf by 1975 totals more than 1.5 million t.N per annum and again Iran and Kuwait will continue to be the most prominent as far as total capacity is concerned, each planning to have between 400,000 and 600,000 t.N.p.a. ammonia capacity respectively operating by the middle of the

next decade. Nevertheless, projects for ammonia and fertilizer plants are also being planned or implemented in three other countries in this area, viz. Saudi Arabia, Iraq and Qatar, and while in size of output these producers will be small compared with either Iran or Kuwait, they will substantially increase the potential export availability of fertilizer and intermediate nitrogen from this area.

[*Nitrogen*, No. 61, (Sept. Oct.) (1969), 15]

Phosphates as Animal Feed in USSR

Lack of adequate levels of the two most important mineral requirements of animals—calcium and phosphorous—in the diet or an imbalance in the ratio can result in disorders such as a aphosphorosis, rickets or infertility. Two types of supplements are available—those derived from animal sources, such as bone flour, meatmeal and fishmeal and those obtained from the chemical processing of phosphate rock or bones.

In the USSR requirements for feed grade phosphates are expected to increase to nearly 600,000 tonnes P_2O_5 in 1970 and at present the main sources of phosphates used in Soviet animal feeds are defluorinated phosphates (DFP), boneflour, and dicalcium phosphate (DCP). It is essential that necessary elements such as calcium, phosphorous and protein to maintain the animal health must be present in the feed in correct ratio. Each in excess can be equally harmful to the animal. An optimal ratio of calcium to phosphorous in feeds is recommended in the Soviet Union. Most suitable supplements to be used in feeds for pigs and poultry are defluorinated phosphates (DFP) and dicalcium phosphate (DCP).

Evaluation of approximate production costs for feed phosphates has also been undertaken. In this evaluation, estimates were obtained of the cost of producing defluorinated phosphate from domestic supplies of rock and the relative costs of producing dicalcium phosphate coupled with defluorinated phosphate were examined. These investigations also included the comparison of feed phosphate production costs using different phosphorus-bearing materials, such as defluorinated phosphate from domestic phosphorites; dicalcium phosphate from phosphoric acid. Cost evaluation of ammonium phosphate and disodium phosphate has also been undertaken.

[*Phosphorus and Potassium*, No. 43, (1969), 19]

High Yielding Varieties of Rice

The introduction of the new high yielding varieties of rice like IR 8 and Peta has brought a significant change in the rice production throughout tropical Asia. During 1968-69 it is estimated 6.7 per cent of the total rice area in south and southeast Asia (in which 9.8% for India) are under the new varieties of rice and their dissemination is expected to increase rapidly. The new varieties represent a potential for increased output per unit of input and can thus be viewed as a technological improvement. Factors influencing the rate and extent of acceptance of new varieties include: (a) water control; (b) degree of plant protection or resistance to insects, rodents and diseases; (c) availability of complementary inputs, including seeds, fertilizers, chemicals and credit facilities; (d) the relative advantage of new over existing varieties, particularly in economic terms; (e) acceptability of the quality of the new grain; (f) the quality of the farm management; (g) the farm institutional structure; (h) the availability of adequate market resources; including drying facilities, storage warehouses and milling equipment; and (i) government institutional structure, incentives and initiative.

Water control will be a major factor influencing the rate and extent of adoption of new varieties. Dry climate with sufficient irrigation is very useful for adopting the high varieties of seed. The overall economic policy of the government also influences the food grain production. For example, (a) taxation on fertilizers (b) a duty electric pumps for irrigation and a higher tax on agricultural wealth. Because of dominant position of rice in both production and consumption, its price policy is of critical importance in the economy of most Asian countries. Higher production of rice may mean a saving in foreign exchange for rice imports. On the other hand, a higher price of rice leads to higher prices for goods other than rice resulting to higher wages for the workers employed in industries. Higher wages mean higher cost of production and for export goods this negatively influences the competitive position of these goods on the world market. This sequence of events would place inflationary pressure on the economy. The objectives of the government on the price policy are to (a) increase production (b) stabilize prices (c) transfer profits or capital to support development of a section and (d) transfer income to raise the living standard of a sector. For most of the countries in Asia today, the major polic

objective is the achievement of self-sufficiency in the production of rice and certain other foodgrains. Self-sufficiency can be achieved by (a) prohibiting imports, (b) transferring area from other crops to rice or (c) increasing rice yield per hectare. It is implicitly assumed by most people that rice self-sufficiency means achieving adequate increases in production through a sustained increase in yield per hectare. The purpose of stabilization policy is to reduce income fluctuations of both producers and consumers for the producers this will serve as a further incentive to production since it lessens uncertainty. Sometimes price incentives may be necessary to sustain the agriculture growth. This conflict between these two objectives can be minimized by a skillful pricing and taxation policy.

Every effort should be made to encourage the adoption of fertilizer responsive varieties and the use of inputs. The rice price policy has to be re-examined as a consequence of production gains and shifts in comparative advantage brought about by the new varieties. As the new varieties spread, efforts are continuing in almost every country to improve the grain quality and disease and insect resistance of these varieties. Stress should be given for irrigation, multiple cropping and better marketing. Most farmers have a very limited amount of capital or credit with which to buy fertilizer and other cash inputs. They can not afford initially to apply even close to the recommended levels and in many cases they are not familiar with the use of these inputs. When the fertilizer price rises on the rice price falls, these small farmers with few resources will have less income and hence less money available for the purchase of fertilizers. A lower rice price or a higher fertilizer price works particularly to the disadvantage of the small producer and will tend to widen the income distribution within agriculture.

The spread of new varieties has increased interest in irrigation and mechanization as well as in the use of cash inputs. A price support on rice or a subsidy on inputs such as fertilizer may encourage the adoption of the new technology but should not be viewed as long-term programmes. Conversely a tax on rice or cash inputs will discourage the use of new technology particularly among the smaller farmers, further widening the income disparity in agriculture. A more equitable arrangement would involve a tax on land rather than on the product on the cash inputs. Taxes or subsidies for irrigation and mechanization should be considered with a view to in-

creasing the utilization of labour and labour productivity in the rural areas.

[*Monthly Bull. of Agricultural Economics and Statistics*, 18 (6) (1969), 3]

TVA: 1968 Report

Tennessee Valley Authority's National Fertilizer Development Centre at Muscle Shoals Alabama is the most extensive facility in USA for developing new fertilizer products and processes and promoting their use throughout the country. Research at the Centre embraces as wide range of chemical, agronomic, engineering and economic studies. During 1967/68 advances were made on several fronts in both laboratory investigations and pilot-plant work.

Twenty-five ultra high-analysis compounds of phosphate and nitrogen were prepared in the laboratory and several appear promising, in particular phosphonitrilic hexamide with a fertilizer grade of 55-92-0. The latter contains four times as much plant food as the average fertilizer currently in use, and both the nitrogen and phosphorus are as readily assimilated by crops as that in common fertilizers; a more practical method of production is being investigated. Studies have been made on materials produced by reaction with air and ammonia; whereas 20-93-0 grade fertilizer was only 20 per cent soluble in water, a new process variation has yielded a slightly less concentrated but much more soluble product. Further studies will be made in large bench-scale equipment. Two high analysis compounds were prepared by reacting phosphorus pentoxide with ammonium hydroxide and these also show considerable potential. Progress has also been made in the production of another key element in fertilizer manufacture, phosphoric acid; 2 new processes yield a concentrated acid containing 40-45 per cent P_2O_5 . A further research subject that is still in the preliminary stage is concerned with urea-ammonium polyphosphate. It was found that prilling in oil gave better shaped and more uniformly sized particles. Typical products, of which 50-75 per cent was urea, ranged from 30-30-0 to 39-13-0, and it seems likely that no conditioning agent would be required for bulk storage. Bench-scale studies made on the direct production of ammonium polyphosphate from wet process acid containing 54 per cent P_2O_5 showed that when a small amount of urea was added, a lower operating temperature gave the desired polyphosphate content and prevented the formation of phosphates not available to crops.

A continuous method for coating with sulphur, sealant and microbicide, to slow down the release of fertilizer nitrogen has been further improved, while in other pilot plant studies work is almost complete on a process producing ammonium sulphate nitrate from ordinary ammonia solutions and sulphuric acids.

TVA encourages the commercial use of new developments by cooperative programmes with industry and land grants universities throughout USA and through technical visitors to the Centre. Nine patents were granted on recent TVA innovations bringing the total to 174. The number of royalty-free licences issued in 1967/68 to interested firms for the use of TVA developments amounted to 25. TVA processes are now used in 455 plants in 39 states. Farm test-demonstrations programme is actively pursued in 35 states, which include fertilizer trial, field demonstrations, demonstration farms and rapid-adjustment farms. TVA continued to send abroad AID-financed teams of specialists to advise governments on various aspects of fertilizer developments.

[*Nitrogen*, No. 60, (1969), 41]

Gas Purification

The Benfield hot potassium carbonate wash process for removing hydrogen sulphide and carbon dioxide from gas streams, developed by the U.S. Bureau of Mines in 1954, has now passed through major improvements. These have taken place in 3 phases. In the first, it has found use in installations handling synthesis gas, town gas, hydrogen, coke oven gas and so on. In the second stage development, several capital cost advantages were possible by the utilization of an additive to increase absorption efficiency resulting in the need for smaller equipment. With the latest development, this process offers further advantages in investment cost and heat requirement.

In its simplest form, the process involves the use of one single-stage absorption column and one single-stage regeneration column for regenerating the lean absorbent solution by heat treatment. For the most efficient gas purification, it requires a system incorporating 3 absorption stages and 3 regenerative stages. In the 3-stage process, it is possible to reduce carbon dioxide concentration down to 0.02 per cent.

In terms of hydrogen sulphide, the efficiency of the 2-stage system is greater than 99 per cent. When using the 2-stage

regenerative system, flash cooling using a steam ejector can substantially reduce steam consumption, which is generally less than that required for the regeneration unit of an amine-based purification operation.

From 1964 onwards the Benfield process was offered in a modified form incorporating the use of an additive to enhance the action of the hot potassium carbonate absorbent. As a result of the increased efficiency, which this additive achieves and also because of the use of higher operative pressure, investment costs were cut by upto 25 per cent by virtue of the reduction in equipment size; in addition, the introduction of a corrosion-inhibitor into the

absorbent solution allowed further investment economies.

[*Nitrogen*, No. 59, (1969), 42]

In a synthesis gas plant based on partial oxidation of heavy liquid petroleum, proposed for ammonia and methanol production facility at Zaluži in Czechoslovakia, C. Otto and Co. have chosen for desulphurization a 2-stage arrangement using BASF Alkazid process and incorporating a steam-hydrolysis section to convert the carbonyl sulphide to hydrogen sulphide. In this process an aqueous solution of alkali salts of amino acids is used to counter-currently wash the cooled gases at the gasification pressure of 4,250 psig.

Hydrogen sulphide is thus removed from the gas stream and then regenerated by heating, the solution being recycled. One advantage of this system in this case is its high operating pressure and the fact that the washing solution is very selective with respect to hydrogen sulphide.

Carbon dioxide, formed during the shift conversion of the carbon monoxide, will be removed by a newly developed triethanolamine wash process, developed by BASF, which is particularly suitable to high pressure systems. Regeneration of the amine can be effected quite efficiently by simple expansion.

[*ibid*, No. 60, (1969), 37]

Errata for Technology, Vol. 7, Nos. 1 & 2

PAPER: "Electron Microscopic Studies of the Pore Structure of some Common Adsorbents and their Modifications for Evaluation of Gas-solid Chromatographic Properties.", by P. C. Banerjee et al.

Page	Col./Line	Read	For
5	3 Table 1	Pore radius, Å	Pore dia. Å
"	"	31	62
"	1 "	Silica gel	Silica ge
"	Fig. 2D	Copper Ammonium Sulphate	Copper Sulphate

PAPER: "Polarographic Studies on the Mode of Ionization and Chelation of Biuret", by M. B. Misra et al.

Page	Col./Line	Read	For
17	Eqn. (IV)	$\bar{i}_d$	$\bar{i}_d$
"	"	[Ao]	[Aa]
17	Eqn. (V)	[Z] _o	[Z]

PAPER: "Absorption Studies on Cobaltic Biuret Complex", by R. M. Sanyal et al.

In Fig. 1, page 13 please read the legends for the curves as:

1. β -Biuret for curve 1
2. α -Biuret for curve 2
3. α -Cobaltic Biuret Complex for curve 3
4. β -Cobaltic Biuret Complex for curve 4

News in Brief

Agro-Industrial Complex in the Gangetic Plain

Vikram A. Sarabhai, K.T. Thomas and M.P.S. Ramani, in a joint paper presented at the Seminar on Nuclear Power held in Bombay during January 17-18, 1970, outlined a scheme for a nuclear-powered agro-industrial complex in the Gangetic plain. In terms of a per capita power consumption of 66.17 KWh/annum, India occupies 113th position in the world, but because of her sheer size she is in a unique position to utilize the benefits of atomic power. With an installed power generation capacity of 9,700 MW in 1966, India had the 14th largest power system in the world and the largest among the developing countries. Since its doubling time is about 7 years, any decision concerning a new generating plant taken now should be in relation to its size by 1975. The authors maintained that a national figure of about 25,000 MW made up of 4 regional grids of 6,000 MW each should be considered.

The proposed nuclear powered agro-industrial complex would cover 3 divisions of Agra, Meerut and Rohilkhand of U.P. A project involving about Rs. 1200 crores in the region would give a return on investment of the order of more than 65 per cent per annum. Low-cost nuclear energy can be used for production of aluminium, for providing water for irrigation either by desalination or by energizing tube wells and ultimately for cultivation of food crops.

[*Nuclear India*, 8 (5 & 6) (1970), 15]

Production in Dry Lands

Dr. M. S. Swaminathan, Director, Indian Agricultural Research Institute, recently outlined at Kharagpur a 10-point integrated strategy to increase agricultural production in unirrigated areas which constitute nearly 4/5th of the total cultivated area in India. The points are: land consolidation and soil conservation, improvements in tillage, addition of organic matter in the form of plant residues to improve the soil, study of rainfall pattern, introduction of 'water-harvesting' procedure, marketability

of produce and general farm economy, study of weather data, intensification of surveys and use of 'remote sensing techniques', problems of malnutrition in dry areas and genetic upgrading of cattle through artificial insemination. The high-yielding varieties programme in wheat which had spread to 4 million hectares as against the target of 2 million hectares by 1969-70 was the first example of a well-planned synergistic inter-reaction in increasing productivity. The breakthrough in agriculture achieved in irrigated areas through the introduction of high-yielding varieties had to be transferred into a revolution by concentrating attention on the dry areas.

[*FAI Inf. Serv.*, 11 (2) (1970), 6]

Fertilizer-Pesticide Mixture

Hindustan Insecticides Ltd., in collaboration with the Fertilizer Corporation of India, is making efforts to evolve a mixed formulation of fertilizer and pesticide. Sprayable fertilizers like urea can be mixed with pesticide to make a mixed formulation to avoid duplication of work in the fields. Such experiments in certain other countries have proved successful. Both the above organizations will be seeking cooperation of the Indian Agricultural Research Institute for field trials.

[*FAI Inf. Serv.*, 11 (5) (1970), 8]

High Yielding Varieties Programme

The overall performance of high yielding varieties programme during *rabi* season 1968-69 covering wheat, paddy and jowar has been encouraging. A significant breakthrough has been made in wheat in physical terms of area coverage but a qualitative breakthrough in terms of reaching the recommended levels of adoption of inputs is yet to be achieved. These observations have been made by Programme Evaluation Organisation of the Planning Commission. Their study covered 32 Blocks and 96 sample villages. The study says that better level of adoption, particularly in terms of adoption of recommended doses of fertilizers in combination with other improved

package of practices, need to be canvassed more vigorously if problems of poor offtake of fertilizers, etc. are to be overcome. This *rabi* season's experience has confirmed the observation made earlier that new varieties of rice, jowar fare better in *rabi* than in *kharif* season. There was significant improvement in levels of achievements in regard to wheat and paddy targets while achievements of targets of *jowar* continued to be low. Among the varieties introduced, Kalyan S-227, S-308 and P.V. 18 varieties of wheat and IR-8 of paddy became popular.

[*Yojana*, 13 (25) (1969), 7]

Nitrogen Pollution in USA

Dr. B. Commoner, Professor of Botany, Washington University, in a report to a Government sub-committee has stated that "the massive use of inorganic fertilizers, especially nitrogen...has already destroyed the self-purifying capabilities of nearly every river in Illinois...and raised the nitrogen level of drinking water supplies in the Midwest and California above the safe limit recommended by the public health authorities". Speaking at a more recent meeting, sponsored by the Soil Association in London, Dr. Commoner put forward a theory that, besides producing a deleterious balance between organic and inorganic soil nitrogen, the use of synthetic nitrogenous fertilizers may be helping to form smog, which is evident in many areas of USA. When land is overloaded with nitrogen, nitric oxides are given off which react with other naturally occurring substances in the air to produce smog. Partly substantiating this claim is the fact that smog has been seen over intensively-formed areas, away from the cities where this phenomenon has been put down to car exhaust fumes.

[*Nitrogen*, No. 62, (1969), 2]

Fertilizer Complex in Iran

Well on the way to completion is the large chemical fertilizer complex currently under construction at Bandar Shahpur at the northern edge of Persian Gulf. The

plant which is to be operated by Shahpur Chemical Co. Ltd—formed in 1965 as a jointly owned subsidiary of National Petroleum Co. of Iran (a Government organization for the development of the petrochemical industry in Iran) and Allied Chemical Corp., New York—makes provision for the production of some 272,000 t.N/yr. as ammonia and around 160,000 t.P₂O₅/yr. as phosphoric acid, together with considerable tonnages of the various fertilizer derivatives, viz. urea, diammonium phosphate, triple superphosphate and complex fertilizers. Sour natural gas from Masjid-Sulaiman oilfields and Moroccan phosphates are the feedstocks and the project features the Allied Chemical-CPI urea process, engineered by Krebs et Cie, a diammonium phosphate plant designed and engineered by the D. M. Weatherly Co. and a 100 tpd ammonia plant designed and engineered by the M. W. Kellogg Co.

Nominal capacity for the ammonia plant due on stream during the second quarter of 1970 in 272,000 t.N/yr. of which one-third is scheduled for 164,000 tpa of urea and a portion is to be used for diammonium phosphate manufacture; the balance will be exported. Sulphur obtained from H₂S removed from the sour gas is sufficient to provide the sulphuric acid feedstock for the wet process phosphoric acid plant. About 500,000 te of sulphur will be recovered annually in a Ralph M. Parsons unit incorporating SNPA amine-wash system, out of which 150,000 te is required for phosphoric acid production, while the remaining 350,000 te will be available for export.

[*Nitrogen*, No. 62, (1969), 35]

Gas Cleaning Process

The construction of a unit to remove sulphur dioxide from flue gases has been completed at the Turaszow power plant in Poland. The process injects gasified ammonia into the stack gas and results in the production of fertilizer grade ammonium sulphate.

[*ibid*, 37]

New Urea Process

Mitruji Toatsu Chemicals Inc. of Tokyo have developed a new urea process of the total solution recycle type giving 0.85 ton of steam consumption for one ton of urea. It is named as total recycle D process. One of its features is the separation of the excess ammonia from the reaction product under high temperature and pressure, which has been made possible by mecha-

nical improvements. The gaseous ammonia from the high pressure absorber is condensed by direct contact with liquid ammonia and recycled to the reactor. The carbamate solution formed under this high pressure is also recycled to the reactor. The liquid with high enthalpy is fed to the synthesis section, where the enthalpy is fully utilized. This system reduces consumption of steam and cooling water.

[*Chem. Age*, 99 (2619) (1969), 21]

Nitric Acid Technology

Simultaneously with Chemico's largest nitric plant using new pollution—abatement technology, Humphreys & Glasgow Ltd. of UK developed a process which eliminates wasteheat boilers and Girdler Corp. 's catalyst which does not contain any noble metal.

The Chemico and H & G modifications are designed around usual ammonia-oxidation/water absorption route to nitric acid. Chemico's dual-combustor process claims nearly complete reduction of nitrogen oxides. Most single combustors have only succeeded in reducing nitrogen dioxide, although a few have been built that carry reduction to completion. Chemico's 2-train process avoids overheating problems common to many single-train units simply by by-passing a portion of trail gas around the first combustor, completing reduction in the second combustor.

H & G's process recovers heat from the ammonia/air oxidation step through an expansion turbine made of high nickel alloy steel. The design calls for carrying out oxidation at about 5 atm, then compressing turbine exhausts gas to over 10 atm prior to absorption with water. The essential difference between this method and the older schemes are use of an expansion turbine to recover heat of combustion directly from hot gases; present methods conventionally employ wasteheat boilers that in turn supply steam to steam turbines. A big advantage is the elimination of steam reboilers, resulting in a simplification of the process flow scheme. This process is particularly suitable for high production rates possibly up to 2,000 tons/day.

Girdler combustion catalyst is a replacement for the conventional platinum/rhodium formulations, thus cutting down one plant's capital investment requirements. Also claimed: longer continuous operation without loss of activity; ability to stand

drastic savings in temperatures; and endurance at high heats.

[*Chem. Engng.*, 76 (27) (1969), 50]

Ammonia Quench Converter

Realising the need for a simple high efficiency converter, ICI have installed recently a new design of converter at Billingham with efficient quench gas introduction/mixing, together with simplicity of construction, catalyst loading, erection and maintenance.

The heart of the new converter is a central heat exchanger surrounded by a single annular bed of catalyst. The cartridge shell containing the catalyst and exchanger is insulated on the outer surface and located in the main pressure vessel. The catalyst forms a continuous bed—allowing easy charging and discharging—with the special gas distributor lying in the catalyst bed. The distributor is so designed that 95 per cent of the synthesis gas passing down through the catalyst bed mixes with the quench gas introduced at intervals down the bed.

The first quench converter was commissioned in early 1969 and was rated for an output of 956 tons/day ammonia with a synthesis pressure 2080 psig. This particular converter was nearly 11 ft. diam. and 40 ft. long but the design can be used for a range of outputs from 600 to 1650 ton/day. Gas distribution within the converter was found to be very uniform. It was charged with about 190 tons of ICI's 35-4 catalyst but not prerduced.

[*Chem. & Proc. Engng.*, 50 (10) (1969), 7]

Gypsum Conversion Process

A new process for the conversion of gypsum to ammonium sulphate and calcium carbonate has recently been developed by Continental Engineering, Amsterdam using waste by-product gypsum and carbon dioxide into a circulating slurry of gypsum in a single reactor. A higher conversion rate has been achieved resulting in lower capital costs and reduced conversion of ammonia. The reactor is so designed that the gases are intensively mixed with gypsum slurry in special mixing devices and dissolve rapidly. One cost advantage is that there is no separate preparation of an initial ammonium carbonate solution.

The reactor is a tall cylindrical vessel in which a slurry of unconverted gypsum, calcium carbonate, ammonium carbonate and ammonium sulphate is circulated. Heat of reaction is removed externally and

fresh gypsum of the correct concentration is continuously fed into the reactor. The carbon dioxide and ammonia are fed through special mixing and rapid dissolution of the gases.

In the filtration section, the calcium carbonate is separated from the ammonium sulphate on a rotating vacuum filter. The first portion of the filtrate is returned to the slurry preparation tank in order to dilute the gypsum before it enters the reactor. The remainder is either concentrated to give ammonium sulphate crystals or used to make complex fertilizer direct.

The ammonium sulphate solution strength (from the filter) is 38-40 per cent, with only 0.8 per cent ammonia. The ammonia concentration in the calcium carbonate cake is 0.5 per cent related to dry cake.

Raw Materials / Utilities Consumption per tonne of Ammonium Sulphate

Ammonia	0.288 t.
Carbon Dioxide	0.368 t.
Gypsum	1.45 t.
Process Water	1.50 t.
Cooling Water (at 15°C)	22 m ³ (5800 gal)
Electricity	25 kWh.

[*Chem. & Proc. Engng.*, 50 (10) (1969),100]

Patents*

Ammonium Nitrate by Srini Vasan (to International Minerals and Chemical Corp.) U.S. 3,476,544, Nov. 4, 1969, Appl. Apr. 12, 1967; 4pp.

A melt comprised of NH_4NO_3 and 7% langbeinite is used as feed to a prilling tower. Thus a molten (250-350°F.) mixture of 80% NH_4NO_3 and 20% langbeinite was fed to a prilling tower. The resulting prills (140-200°F) were cooled in a rotary cooler. Such products remain free-flowing without adding an anti-caking agent. The rate of dissolution of the langbeinite in H_2O is increased by co-prilling.

[*Fertilizer Abstracts*, 3 (1) (1970), 1]

Concentrating Nitric Acid by C. D. Miserlis

*These patents have been reproduced from *Fertilizer Abstracts* published by the National Fertilizer Development Centre, TVA, Muscle Shoals, Alabama (USA) with kind permission of Editor FA. —Editor.

(to Badger Co., Inc.) U.S.3,479,254, Nov. 18, 1969, Appl. May 22, 1967; 4pp.

A two-stage distillation process for concentrating HNO_3 is described. The first stage is carried out at subatmospheric pressure and non-azeotropic conditions. Feed for the first stage consists of 70% HNO_3 prepared by mixing incoming 55% HNO_3 with recycled overhead from the first stage and bottoms from the second stage. The feed enters the midsection of a column-still maintained at a bottoms pressure of 400 mm Hg absolute and a bottoms temperature of 220°F. The overhead vapors leaving the column are condensed yielding 99.6% HNO_3 of which a portion is returned as reflux, a portion is recycled to the feed, and the remainder is withdrawn as product. Bottoms from the first stage, having an azeotropic concentration of 67% HNO_3 , are fed to the second stage distillation column which is operated at a bottoms pressure of 1200 mm Hg and a temperature of 275°F. The overhead vapors from the second stage consist of H_2O , a portion of which is returned as reflux and the remainder is discharged from the system. The second stage bottoms, comprised of 69% HNO_3 , are recycled to the first column feed. The first stage is superimposed on the second stage in a single column. The overhead vapours from the second stage are the source of heat for the bottoms reboiler in the first stage.

[*ibid*, *idm*]

Manufacture of Nitric Acid by D. M. Fletcher and M. M. Wendel (to E. I. de Pont de Nemours, and Co.).

U.S. 3,475,118, Oct. 28, 1969 Appl. Nov. 1, 1966; 5 pp.

A process is described in which acid containing 40-65% HNO_3 and acid containing 65% HNO_3 are produced as co-products. The main novelty consists of feeding to the bottom of an absorption column a gas mixture containing 1% H_2O and 5-10% N oxides whose state of oxidation is 95%, and preferably 98%. A sidestream containing 40-65% HNO_3 is withdrawn from an intermediate part of the column in an amount corresponding to 12% of the total moles of reactive N oxides in the feed. Acid containing 65% HNO_3 is withdrawn from the base of the column. Thus, a gas mixture containing NO_2 ($\text{NO}_2 + \text{N}_2\text{O}_5$) 6.8, NO 0.1, and 04.2% volume and 0.4% wt H_2O was prepared by usual methods from the products of NH_3 oxidation. The gas mixture was fed at 103,394 lbs/hour to the base of a 10.5 ft.

diameter absorption column fitted with 35 water-cooled bubble cap trays spaced 1 ft. apart. Water was fed to the top of the column at 9406.5 lbs/hour. The temperature in the column was maintained at 25° and the pressure at 90 lb. sq. inch gage. Product acid containing 60% HNO_3 was withdrawn from the 12th tray at 5026.5 lbs/hour. A second product acid containing 68% HNO_3 was withdrawn from the bottom tray at 17,313 lbs/hour. Tail gas was produced at 90,461 lbs/hour containing 0.3% volume N oxides. The yield was 96.8%. Other examples give data from similar tests producing acid containing up to 80% HNO_3 . The process can be adapted to existing plants without sacrificing yield or capacity. It allows production acid containing 65% HNO_3 without refrigeration or dehydration.

[*ibid*, *idm*]

Urea Synthesis by a Total Recycle Process by Mario Guadalupi (to SNAM S.p.A.) U.S. 3,370,247, Sept. 30, 1969, Appl. Italy Sept. 8, 1964; 5 pp.

A process is described in which a urea synthesis autoclave is charged with fresh NH_3 and CO_2 along with recycle product in the form of $\text{NH}_4\text{NH}_2\text{CO}_2$ in aqueous ammoniated solution in such proportions that the $\text{NH}_3:\text{CO}_2$ mole ratio is higher than 2:1. The reaction product is then removed and allowed to expand in a separator at pressures in the range 150-100 kg/sq cm. so as to liberate a substantial portion of the unreacted NH_3 . The resulting material, thus freed of an important fraction of the unreacted NH_3 , is sent to a primary decomposer for the $\text{NH}_4\text{NH}_2\text{CO}_2$ where, at pressures of 120-80 kg/sq. cm, the $\text{NH}_4\text{NH}_2\text{CO}_2$ is partially decomposed. The mixture is then sent to a stripper in which, at pressures of 120-80 kg/sq cm, there is blown countercurrent to the mixture the gaseous NH_3 separated earlier in the expansion stage, while simultaneously maintaining the heat balance favorable for completing the decomposition of the $\text{NH}_4\text{NH}_2\text{CO}_2$ into NH_3 and CO_2 . The resulting urea solution which contains in addition virtually only NH_3 is then expanded in one or more stages, steam and NH_3 being thereby liberated. The steam and NH_3 are condensed at 15-20 kg/sq cm. and recycled in the form of ammoniated solution. Ammonia and CO_2 from the preceding decomposition of $\text{NH}_4\text{NH}_2\text{CO}_2$ are absorbed by the aqueous ammoniated solution, thereby forming an ammoniated solution of $\text{NH}_4\text{NH}_2\text{CO}_2$. The heat of formation of the $\text{NH}_4\text{NH}_2\text{CO}_2$ is utilized for producing steam

on account of the higher thermal level at which the heat becomes available. The high pressure at which NH_3 and CO_2 are available allows absorption at high temperatures (above 150°), thereby differing from other urea processes where absorption is carried out in more stages and at lower pressures. It is therefore possible to carry out the recycling of NH_3 and CO_2 with a relatively small amount of water and with a relatively low power requirement.

[*ibid idm*]

Preparing Ammoniated Nitric Acid-Phosphate Rock Extracts by A. V. Slack (to Tennessee Valley Authority) U.S. 3,477,843, Nov. 11, 1969, Appl. Jan. 16, 1967; 20 pp.

Addition of a relatively small amount of soluble acyclic polyphosphate compounds to partially ammoniated HNO_3 -phosphate rock extracts prevents precipitation of apatite and other unavailable phosphates during the subsequent ammoniation to neutrality. The precipitated phosphate is almost entirely in the form of CaHPO_4 . A suitable polyphosphate for use in this process is ammoniated superphosphoric acid containing 11% N and 37% P_2O_5 (11-37-0). Another suitable additive is $\text{Na}_5\text{P}_3\text{O}_{10}$. The additive is used in amounts to supply about 10 to 20% of the total P_2O_5 contained in the final product. The extract is partially ammoniated to a pH of about 1.9 to 2.5, the additive is then* introduced, and ammoniation is especially useful in the manufacture of fluid fertilizers containing solids in suspension.

[*ibid*, 2]

Nitrophosphate Process by R. L. Abbott and L. A. Stengel (to Commercial Solvents Corp.) U.S. 3,475,153, Oct. 28, 1969, Appl. May 12, 1966; 3 pp.

Phosphate rock is digested with HNO_3 by usual methods. The resulting slurry containing insoluble impurities from the rock is then treated with a soluble sulfate in an amount sufficient to precipitate only a minor portion of the Ca as CaSO_4 . The precipitated CaSO_4 serves to coagulate the insoluble impurities which are then removed by filtering or centrifuging. The clarified solution is then treated with additional soluble sulfate in an amount sufficient to precipitate substantially all of the remaining Ca as CaSO_4 which is then removed from the solution. The clarified solution is then ammoniated by usual methods to prepare a solution containing NH_4NO_3 and ammonium phosphate. The

solution is used to prepare fertilizers. The soluble sulfate can consist of H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$. The process makes possible the separation of insoluble impurities in readily filterable form. The second precipitate of CaSO_4 is recoverable in commercially useful form. The product is substantially free of $\text{Ca}(\text{NO}_3)_2$.

[*ibid*, 6]

Granular Fertilizers, by Bernard Quanquin, G. M. LeClerc, and Jean-Louis Pierre (to Potasse et Engrais Chimiques). U.S. 3,475,195, Oct. 28, 1969, Appl. Fr. Dec. 1, 1964; 6 pp.

A melt or slurry of fertilizer material is granulated by spraying it onto falling fines in the presence of a flow of gases. Fines are fed into the top of a cylindrical vessel having a vertical axis and fall by gravity. The slurry to be granulated is sprayed downwardly through the falling fines from a nozzle in the upper portion of the vessel and also upwardly from another nozzle in the lower portion of the vessel. The axis of the two opposing conical sprays is parallel to the axis of the cylinder. The top of the vessel is surrounded by an annular chamber provided with inlet ducts for the drying or cooling gas. The gas flow is downward through the vessel, cocurrent with the flow of solids. The gas leaves the bottom of the vessel carrying solids in suspension, the mixture is passed through a separator which removes the solids, and the fines are separated and returned to the granulation vessel.

[*ibid*, 7]

Coating Fertilizer Granules, by L. H. Cook and Sydney Atkin (to Chemical Construction Corp.). U.S. 3,477,842, Nov. 11, Appl. Oct., 10, 1966; 4 pp.

An anti-caking treatment for granular fertilizer consists of coating the granules with an aqueous alkaline (pH 7.5-10) solution containing urea and formaldehyde (mole ratio 0.75-0.85:1) followed by drying. Thus, a solution was prepared by dissolving 56g urea crystals in 100 g aqueous 37% formaldehyde solution. The pH was then adjusted to 8.5 with NH_4OH and the solution was sprayed on a mass of urea crystals. The crystals were dried; they remained uncaked and free-flowing after one year of storage.

[*ibid*, 8]

Production of Hydrogen by W. C. Pfefferle (to Engelhard Industries, Inc.). U.S. 3,481,722, Dec. 2, 1969, Appl. May 15, 1964; 5 pp.

A two-stage process is described for the production of H by steam-reforming of normally liquid hydrocarbons. In the first stage a mixture of the hydrocarbon with steam and added H is contacted with a Pt-group catalyst at a temperature below 700° (preferably about 625°). The effluent from the first stage is then contacted with additional catalyst at a temperature between 700 and 1000° .

[*ibid*, 3 (3) (1970), 49]

In situ Acidulation of Phosphate Rock, by E. W. Biederman (to Cities Service Oil Co.). U.S. 3,490,811, Jan. 20, 1970, Appl. July 8, 1968; 3 pp.

Phosphate rock is acidulated *in situ* by injecting H_2SO_4 , HNO_3 , or HCl into an underground deposit through an injection well. The H_3PO_4 solution formed by reaction of the phosphate rock and the injected acid is brought to the surface through a series of production wells by injection pressure. At the surface the H_3PO_4 solution is processed by usual methods to prepare commercial H_3PO_4 or phosphatic fertilizers. If deposition of insoluble reaction products causes undesirable decrease in the permeability of the deposit this problem is overcome by increasing the injection pressure to cause fracturing of the deposit.

[*ibid*, *idm*]

Aqua Ammonia, by Jonathan Garst, U.S., 3,468,134, Sept. 23, 1969, Appl. Aug. 4, 1967; 5 pp.

In shipping NH_3 by refrigerated vessels, a small amount of water is added to the NH_3 as it is being loaded. At the point of destination all that is necessary is to connect a line from a dockside source of water to the line from the vessel. The resulting 20% N solution can then be pumped by the pump on the vessel directly to non-pressurized and nonrefrigerated storage.

[*ibid*, 3 (4) (1970), 71]

Removing Magnesium from Phosphate Rock, by W. R. Bosen, R. B. Humberger, J. L. Smith, and C. M. Davis (to J. R. Simplot Co.) U.S., 3,493,340, Feb. 3, 1970, Appl. June 29, 1965; 11 pp.

When Mg-containing phosphate rock is used to manufacture H_3PO_4 by the wet process the product acid is contaminated with Mg. If the $\text{MgO}:\text{P}_2\text{O}_5$ wt ratio in the acid is 0.01:1 objectionable sludge is formed when the acid is used to manufacture NH_4 phosphate or NH_4 polyphosphate fertilizers. A method is described for pre-

treating the phosphate rock with an acidic leach solution which removes much of the Mg without removing significant amounts of P_2O_5 from the rock. The treated rock is then used to manufacture H_3PO_4 in the usual way. Thus, phosphate rock was calcined at 1400-75°F., cooled, and ground to 65%-200 mesh. The prepared rock contained P_2O_5 31.8-32.0, CaO 45.5, and MgO 0.65%. A slurry was prepared by mixing 80 g rock with 800 ml distilled H_2O . The equilibrium pH of the slurry was 10.98. A 6.104N H_2SO_4 solution was added until the pH reached 3.0, and the pH was held at 3.0 ± 0.15 for 1 hr. by periodic additions of H_2SO_4 . The mixture was then filtered. The filtrate contained 74% of the MgO; the solids contained 99.64% of the P_2O_5 .

[*ibid*, 72]

Purifying Phosphoric Acid, by J. N. Carothers and R. J. Hurka, U.S. 3,494,736, Feb. 10, 1970, Appl. Oct. 22, 1965; 4 pp.

Wet-process phosphoric acid containing Si, F, and Al is treated with Na^+ and F^- under conditions resulting in precipitation of substantially all of the Si as $Na_2 SiF_6$.

Sufficient Na^+ is added (as carbonate or orthophosphate) to provide two moles Na^+ /mole fluosilicate ion and 0.5 part Na^+ /100 parts acid. The precipitate is removed, and the acid is then treated with Na^+ and F^- under conditions resulting in precipitation of substantially all the Al and F as crystalline $Na_3 AlF_6$ of commercial purity. Sufficient F- is added as NaF or HF. The purified acid contains a small amount of Na^+ which is not objectionable for most uses.

[*ibid*,]

Concentrating Phosphoric Acid, by C. W. Putnam. U.S., 3,467,162 Sept. 16, 1969, Appl. July 11, 1966; 6pp.

In concentrating wet-process H_3PO_4 to about 54% P_2O_5 by usual methods the impurities precipitate as very small particles. This can cause the acid to become noticeably viscous. In any case the fine particles are difficult to remove from the acid. Precipitation of the impurities in small particle sizes is prevented by conducting the concentration in such manner as to avoid sharp changes in temperature or concentration. Supersaturation is thereby avoided and the impurities form large particles. Provision is made to mix the acid at the evaporating surfaces quickly back into the bulk of the acid in the evaporator. Similar provision is made to avoid

sharp changes in concentration in adding feed acid. Application of this principle to submerged combustion, falling film, or vacuum evaporators is described. The method also decreases post-precipitation of impurities.

[*ibid*, 73]

Phosphate Fertilizers, by A. G. Betts U.S., 3,489,510, Jan. 13, 1970, Appl. June 5, 1968; 7 pp.

A superphosphate-type fertilizer in which the P_2O_5 is mainly in the form of $CaHPO_4 \cdot 2H_2O$, no F is evolved during manufacture, and less acid is required per unit of available P_2O_5 , is produced by acidulating phosphate rock in the presence of $Al_2(SO_4)_3$. The $Al_2(SO_4)_3$ can be added as such or it can be produced by acidulating ores such as bauxite or leached-zone phosphate. The proportions are such that the reaction mixture contains 1.3 to 1.8 parts Al_2O_3 per part of F. For example, 10.2 parts of bauxite containing 50% acid-soluble Al_2O_3 was treated with hot H_2SO_4 solution containing 42 parts H_2SO_4 . To the resulting solution of H_2SO_4 and $Al_2(SO_4)_3$ was added with stirring 100 parts of finely ground phosphate rock containing P_2O_5 32.8, CaO 47.8, and F 3.9%. The mixture was held at 90° for two days with periodic additions of water in amounts required to maintain a thick slurry. The slurry was then dried, yielding 170 parts of product containing about 45% $CaHPO_4 \cdot 2H_2O$ and 40% gypsum. If H_3PO_4 is used for acidulation, the $Al_2(SO_4)_3$ can be added to the H_3PO_4 before mixing with the phosphate rock. In this case the product will contain about 16% gypsum.

[*ibid*, 74]

Ammonium Polyphosphate Solutions, by R. R. MacGregor, A. J. Stanley, and W. P. Moore (to Allied Chemical Crop.) U.S. 3,492,087, Jan. 27, 1970, Appl. July 26, 1966; 4 pp.

Ammonium polyphosphate solutions suitable for fertilizer use are produced by reacting NH_3 with wet-process H_3PO_4 in a two-stage countercurrent reactor, followed by dissolving the melt and filtering. The first stage is preferably carried out at 140°, atmospheric pressure, and a pH of not over 2.2. The second stage is preferably carried out at 260°, a pressure below 2 atmospheres, and a pH of 2.6-4.2. The melt from the second stage is dissolved in aqua ammonia at about 50° to raise the N content to 10-12% and the pH to about 6. The solution is then filtered, giving a clear

solution containing 30-70% of the p_2O_5 in polyphosphate form.

[*ibid*, 76]

Reduction of Phosphate Rock, by W. C. Saeman (to Olin Mathieson Chemical Corp.) U.S. 3,479,138, Nov. 18, 1969, Appl. Sept. 22, 1964 and Mar. 18, 1968; 7 pp.

Phosphorus values are recovered from phosphate rock by feeding phosphate rock, coke, and SiO_2 to a rotary kiln having a vitreous lining held in place centrifugally. The kiln is direct fired to maintain a reaction zone temperature of 2800-4200°F.

[*ibid*, 3 (2) (1970), 24]

Phosphorus by P. L. Veltman and P. G. Imperiale (to W. R. Grace & Co.) U. S. 3,381,706, Dec. 2, 1969, Appl. Dec. 28, 1967; 7 pp.

Elemental P is produced by passing phosphate rock through a flame in the presence of a reducing gas. Thus, —200 mesh phosphate rock was fed at 28 tons/hour to a fluidized bed preheater heated by gases from a later step. Rock at 1700°F from the preheater was mixed with natural gas and the mixture was fed into the top of a reactor. The reactor was comprised of a vertical cylindrical carbon-steel shell 2.5 ft. I.D. $\times$ 100 ft. high lined with cast SiO_2 refractory 6 inches thick. A 4000°F flame produced by combustion of natural gas with commercial 95% O was maintained in the upper part of the reactor by a plurality of burners. The gaseous products containing molten slag droplets were passed through a cyclone where the slag was separated. The effluent gases at 3200°F were passed through the fluidized bed preheater and then through a waste heat boiler. The gases leaving the waste heat boiler were cooled to condense and separate elemental P. Addition of 10% of the total heat by imposition of an electric current on the flame is desirable for maintaining uniform temperature in the reactor.

[*ibid*.]

Phosphoric Acid and Calcium Aluminate, by W. P. Moore and R. R. MacGregor (to Allied Chemical Crop) U.S. 3,482,933, Dec. 9, 1969, Appl. Jan. 24, 1967; 6 pp.

In a process for producing H_3PO_4 from HCl and phosphate rock the by-product $CaCl_2$ is converted to calcium aluminate and HCl, the HCl being recycled to the acidulation step. Thus, - 50 mesh phosphate rock containing P_2O_5 31.2, CaO 45.5, and SiO_2 7.8% wt. was mixed at 161.9 lb/hour with 485.8 lb/hour water. The resulting

suspension was fed continuously to a countercurrent acidulation system comprised of a series of three acid-brick lined towers one ft. diameter $\times$ 8 ft. high. A gas mixture at 400° containing HCl 4.9, H₂O 27.7, CO₂ 11.3, and N 56.1% wt. was also fed to the system at 2265.9 lb/hour. Temperatures in the three towers were 98, 94, and 91° respectively and pressures were essentially one atmosphere. Acidulation slurry containing H₃PO₄ 8.8, HCl 0.6, CaCl₂ 18.6, SiO₂ 1.1, and H₂O 65.8% wt. was discharged from the system at 786.8 lb/hr. The slurry was filtered, and the filtrate was extracted with 900 lb/hr. isoamyl alcohol. The organic phase was separated and washed with H₂O to produce 81.7 lb/hr. 80% H₃PO₄. The aqueous phase containing 22.8% CaCl₂ was fed at 794.5 lb/hr to a fluidized bed reactor also fed with 164 lb/hr alumina sand containing 88.2% Al₂O₃ and 7.8% SiO₂. The temperature in the reactor was maintained within a few degrees of 850° by combustion of natural gas. Solid product containing CaAl₂O₄ 85.6, CaSiO₃ 0.8, Al₂O₃ 4.7, and P₂O₅ 1.2% wt. was withdrawn from the reactor at 262 lb/hr. On mixing with an equal amount of CaO a product similar to Portland cement was obtained. Gaseous products from the reactor were passed through a cyclone separator and then through a heat exchanger in which air for combustion and fluidization was preheated to 450° and the gas was cooled to 400°. The gas was then recycled to the acidulation towers for treating phosphate rock.

[*ibid*, 27]

Potassium Phosphate Fertilizers by Gulf Research & Development Co. Brit. 1,172, 752, Dec. 3, 1969, U.S. Appl. Sept. 9, 1966; 8 pp.

A mixture of KCl, H₃PO₄ and H₂SO₄ is heated at 130 to 200°, followed by removing residual HCl from the reaction mixture at subatmospheric pressure while sparging steam through the material. The product can be ammoniated to obtain solid N-P-K- fertilizer. For example, 245 g KCl and 865 g wet-process phosphoric acid containing 23.8% P and 1.5%S were vigorously mixed together at a pressure of about 50 mm Hg absolute and a temperature of 107°. Steam and HCl were evolved, leaving a viscous material that solidified on cooling. The material contained 1.9% Cl, 50%P₂O₅, and 16.4% K₂O. It was reheated to 107° and steam was blown through the melt, thereby decreasing the Cl- to less than 0.2%. The resulting solid product was readily ammoniated to obtain

a hard, easily-pulverized, non-hygroscopic solid containing 9%N.

[*ibid*, 30]

Lightweight High-Analysis Fertilizers, by A. M. Murphy, F.A. Retzke, and J. R. Johnson (to Borden Co.) U.S. 3,479,175, Nov. 18, 1969, Appl. Nov. 7, 1966; 3 pp.

The title products are made by heating a dry mixture of urea, dry source of formaldehyde, and P and K fertilizer materials and extruding the hot mixture. For example, a dry mixture was prepared from 1436 lb of ground urea, 189 lb of (NH₄)₂HPO₄ from furnace grade acid, 339 lb of KCl, and 41 lb of finely ground paraformaldehyde. The mixture was fed at 300 lb/hour to a jacketed screw conveyor. The mixture left the conveyor at 150°F and was fed to an auger-type pin barrel extruder having a die plate with 320 one-eighth inch diameter holes. The extruded material left the die plate at 165°F. It was cut into pellets by a rotating wire and screened at 140°F to obtain a -6+10 mesh product having a bulk density of 38 lb/cu ft. The product grade was 35.2-5.5-9.9. Other examples describe the preparation of 30-10-10, 30-5-8, 25-10-5, 24-8-8, and 33-5-10 grades by similar procedures.

[*ibid*, *idm*]

Ammonium Polyphosphate Fertilizers, by T. D. Farr, H. K. Walters, and J. D. Fleming (to Tennessee Valley Authority). U.S. 3,484,192, Dec. 16, 1969, Appl. Aug. 24, 1967; 20 pp.

Solid or liquid fertilizers containing ammonium polyphosphates are produced by a stepwise ammoniation of superphosphoric acid at atmospheric pressure. In the first step the conditions in the ammoniator are regulated to maintain the temperature between 50 and 80°, the pH between 5 and 7, and the concentration of N + P₂O₅ above 33%. In the second step the conditions are regulated to maintain the temperature between 50 and 110°, the pH between 7.4 and 8.9, and the concentration of N + P₂O₅ above 50%. The reaction product can be dried and granulated to prepare solid fertilizers containing 17-21% N and 52-60% P₂O₅ or it can be filtered to obtain solid fertilizers containing 20.6-20.9%N and 55.4-57.0% P₂O₅ and a filtrate which is recycled. In an example, superphosphoric acid (77%P₂O₅), NH₃, and water were combined at 70°, forming a stock solution at pH 5.8, containing 11.1% N and 37.6%P₂O₅. The P₂O₅ was present as 37% ortho-, 46% pyro-, 15% tripoly-, and 2%

trtetra polyphosphate. Part of this solution was ammoniated at 15-20°, to prepare a slurry having a pH of 8.5 and a viscosity of 600 centipoises. The slurry was vacuum filtered at a rate of 100 lb/hour/sq ft. The solids were dried. The filtrate was mixed with a portion of the stock solution and the mixture was ammoniated as before to pH 8.5, and filtered. The cycle was repeated three times. The four solid products contained 20.6-20.9%N and 55.4-57.0% P₂O₅; the P₂O₅ was present as 34-42% ortho-, 48-56% pyro-, 8-10% tripoly-, and 1% tetrapolyphosphate. The four filtrates contained 11.2-11.5% N and 30.4-30.9%P₂O₅.

[*ibid*, 31]

Utilization of Polyphosphates in Dried Milk

Under a commission set up recently by the International Dairy Federation, experiments were conducted to examine the use of polyphosphates as an anticoagulant in bulk stored dried milk. It was concluded that from a technological point of view it is very useful to permit the addition of polyphosphates alone or together with monophosphates to milk powder, although it was, felt not to fully recommend their use.

The experiments showed that there was no difference in toxicity between mono- and polyphosphates but that in cases where high dosages were used both were harmful to animal and human health. Levels of tolerance of these products varied according to the tests undertaken. It was generally agreed following various experiments that no facts could be derived against the allowance of 0.3% polyphosphates (as anhydrous substances) in milk powder.

[*Phosphorous and Potassium*, No. 43 (1969), 50]

Plant Breeding at the Atomic Energy Commission

The Biology Division of the Bhabha Atomic Research Centre is engaged in plant breeding programmes. It has evolved 6 groundnut mutants which are being tested at several centres through the All-India Oilseeds Research Projects. In collaboration with the Central Rice Research Institute, it has isolated short dwarf and early flowering mutants of rice. Four slender grain mutants TR-6 to TR-9 have been included in the Slender Grain Varietal trials conducted by the All-India Coordinated Rice Improvement Project.

Research programmes on basic and applied aspects of cellular metabolism and the development of food irradiation procedures is being conducted by the Bioche-

mistry and Food Technology Division of BARC. During the year, it continued experimental programmes on the development of promising radiation preservation procedures for perishable foods. Large scale feasibility trials on disinfestation of wheat, extension of storage life of onions and preservations of fish and fish products are in progress at the Food Irradiation and Processing Laboratory.

[*Nuclear India*, 8 (9) (1970), 2]

Underground Plastic Pipe Irrigation

A sprinkler-type irrigation system for citrous-fruit plantations is in operation in an experimental 125 acre project on the Isle of Pines of Cuba. The system uses underground plastic pipes and semi-automatic valves. The new method has a greater man-land area productivity than that obtained previously with the portable aluminium pipes and can be expected to last about 30 years. Also, it allows continuous spraying with all the advantages obtained in night spraying in water savings and distribution due to the reduced wind speed at the time and reduced evaporation because of lower night time temperatures. This method of sprinkling from buried pipe is recommended for use in growing citrus-fruit plantations and allows for an alternate system of irrigation that sprays the water below the foliage of the trees.

[*Cuba*, Feb:March, (1970), 182.]

Gujarat Aromatic Project

The Rs. 22 crores aromatic project, the first of its kind in India, being set up near Baroda as a constituent part of the Indian Petrochemicals Corpn. Ltd., will comprise when commissioned in 1972 five plants viz. catalytic reforming, ortho- and para-xylene, isomerization and DMT plants and will produce 21,000 te/yr orthoxylene, 2500 te/yr mixed xylenes and 24,000 te/yr DMT dimethyl terephthalate. These intermediate products will be further processed into final consumer goods by private sector petro-chemical industries viz., Herdillia Chemicals Bombay, Suhrid Geigy Baroda, Durgapur Chemicals, Indian Organic Chemicals Madras, Swadeshi Cotton Kanpur, Calico Mills Baroda, Chemicals & Fibres (India) Bombay, etc. The phthalic anhydride plants in existence and those under planning or expansion add up to a firm demand in excess of the estimated production of orthoxylene from this project. In addition to the Aromatic Project, the Indian Petrochemicals Corpn. Ltd. will put

up a number of other projects, viz. olefine plant (Rs. 30 crores), naphtha cracker having a capacity of 100,000 tonnes of ethylene and will produce a variety of intermediate products.

The plant will be fed from the existing Koyali refinery and about 70 per cent of the total equipment necessary will be indigenous. Engineers India Ltd., will build the project, which is a part of the Rs. 200 crores Gujarat Petrochemical complex.

[*Lok Udyog*, 3 (12) (1970), 1439]

Slow-Release Fertilizer

Guanyl urea, a new high analysis, slow-release fertilizer, developed after two years of study in Japan, is being introduced to Japanese agriculture. Guanyl urea is produced from the cyanamide contained in calcium cyanamide, by polymerization, extraction with dicyanamide, and then by acid hydrolysis of dicyanamide. The product commonly takes the form of either guanyl urea sulphate or guanyl urea phosphate, and features strong adhesion to the soil and hard water solubility, which make it extremely suitable as a slow-release fertilizer for paddy-fields.

[*Nitrogen*, No. 61, (1969), 40]

ONGC Exploration Programme

The Oil and Natural Gas Commission has drawn up a tentative 10-year oil exploration programme (1969-70 to 1978-79) with an estimated expenditure of about Rs. 1200 crores to explore as much of the country's reserves of oil and gas as possible so as to substantially reduce the gap between the supply and demand of petroleum in the country. Of the above expenditure, Rs. 403 crores are to be spent during IV Plan and Rs. 805 crores during Fifth and Commission expects to earn Rs. 850 crores from the sale of crude and natural gas. The deficit of Rs. 350 crores will be wiped off in $3\frac{1}{2}$ years following the 10-year programme.

Under the programme, commission will carry out geological and geophysical surveys and drilling to discover oil reserves to achieve a production of 14.5 million tonnes annually around 1978-79.

The increase in production is proposed to be achieved in stages. By 1973-74 the Commission envisages an annual production of 6.7 million tonnes on land. Production on land will be stepped up to 10 million tonnes annually by 1978-79. The balance of 4.5 million tonnes of oil is expected to be produced from the current

off-shore drilling in Cambay and high seas of Bombay.

[*Lok Udyog*, 4 (2) (1970), 194]

Indian Consortia for Supplying Plants

A new public sector company, viz. Indian Consortium for Industrial Projects Pvt. Ltd., having as members the following public sector companies, viz. HEC Ranchi, Mining & Allied Machinery Corpr. Ltd., Durgapur, Bharat Heavy Plates & Vessels Ltd. Visakhapatnam, Hindustan Steel Works Construction Ltd. Calcutta, Triveni Structural Ltd. Naini, Bharat Heavy Electricals Ltd. New Delhi, Heavy Electricals (India) Ltd. Bhopal and Instrumentation Ltd. Kota, has been registered. Its objects are to carry on in India and abroad all businesses and their ancillary services and also erection and commissioning thereof, on a turnkey basis or otherwise.

[*Lok Udyog*, 4 (2) (1970), 170]

Naphtha-Reforming Catalyst

Faced with the necessity of the presence of mobile alkali, the inevitability of its loss, and hence the necessity of an adequate reservoir of alkali and desirability of reducing alkali loss to the minimum consistent with satisfactory resistance to carboning up, the catalyst formulator has a difficult task. Many combinations of different alkali levels on different ceramic supports have been tried in an attempt to get best spectrum of properties for the catalyst. The approach in formulating the naphtha-reforming catalyst 46-1 is to use support containing a non-volatile constituent which during the operation of the reformer very slowly decomposes, liberating mobile alkali. This constituent is Kalsilite, KAISiO_4 , which reacts slowly with the carbon dioxide to liberate potassium carbonate. Other potassium compounds also decompose under reforming condition, but generally their rates of decomposition are unsuitable, either too fast leading to excessive loss of potash or too low, in which case the mobile alkali level on the nickel is too low and catalyst will not operate at low steam ratios. Potash loss is thus reduced to the minimum even with a catalyst containing a large quantity of potash by employing what might be termed a "slow release potash reservoir". Kalsilite can readily be made by firing together an intimate mixture of china clay and potash at temperature of over 750°C.

It was found that by typically employing 3/4 charge of this alkalized catalyst (46-1) in the first part of the tube and a 1/4 charge

of the non-alkalized catalyst (ICI 46-2) in the bottom part of the tube allowed tube throughputs to be increased by about one-third for any particular set of exit temperatures and gas compositions. No reduction in the ability to withstand carboning up was noticeable. Two-zone catalyst charge of this type has now become common in commercial plants during the past two years.

[*Indus. and Engng Chem., Prod. Res. & Develop.*, 8 (3) (1969), 321]

Demand for Petroleum Products

The Indian Institute of Petroleum has revised its earlier estimates of demand for petroleum products prepared in February 1968. According to their present estimate, the total refinery capacity in 1973 will be 28.7 million tonnes, about 2 millions more than the capacity provided for in the Plan. The demand is estimated to go upto 31.7 million tonnes by 1974 and 34.1 million tonnes by 1975. This calls for an additional 7.3 million tonnes of refinery capacity by 1975 over the anticipated to be in operation by 1973. The Institute has, therefore, recommended the setting up of a new 3 million tonnes oil refinery in North India before 1974 and the expansion existing refineries to cover the deficit.

[*Oil Statistics*, 7 (3) (1969), 21]

New Fertilizer Policy

Government of India has decided that all fertilizer projects based on imported ammonia in future will be reserved for the public sector. It has approved the expansion of public sector projects at Trombay and Cochin, which are based on imported ammonia. FCI Ltd has already signed an agreement for import of one million tonnes of ammonia from Iran and 5 lakh tonnes from Kuwait over a 7-year period. It has also directed that a feasibility report should be prepared for a public sector plant at Paradeep (Orissa) based on imported ammonia.

[*FCI News*, 8 (3) (1970), 19]

Aerial Application of Urea

In order to improve domestic food production, aerial fertilizer application in India has recently taken place in Punjab. Urea was used on an experimental basis, and should these trials prove successful, the tests will be extended to other areas. Wheat field in these areas are also being sprayed with insecticide against possible pyrrilla attack.

[*Nitrogen*, No. 63 (1970), 4]

New Urea-Based Fertilizer

At the Veszprem (Hungary) chemical industry research institute, production techniques for the manufacture of a new fertilizer, Calurea, have been investigated. The product, obtained from binding urea with calcium nitrate, has been used in field trials and found to be extremely effective under some conditions. Such a fertilizer appear to have certain advantageous neutralizing effects on acidic soils.

[*Nitrogen*, No. 63, (1970), 34]

FCI's Contract with Montecatini

A supplier's credit contract for the supply of imported synthesis and urea sections of the 2 coal-based fertilizer plants to be set up at Talcher and Ramagundem was signed on 20.11.70 between Fertilizer Corporation of India and M/s Montecatini Edison of Italy. The ammonia synthesis and urea section of these plants are based on Montecatini processes for which know-how has already been acquired by the FCI. The Corporation has also obtained know-how for the Kopper-Totzek process for gasification of coal and Rectisol process for gas purification from two W. German firms.

[*Fert. Digest*, 9 (1) (1970), 28]

FCI Acquires NPK Process Licence

A contract between FCI and M/s Stamicarbon of the Netherlands for collaboration of licence and know-how for producing NPK fertilizer from nitrophosphate route was signed on November 8. The know-how will be used in the expansion programme at Trombay and at Haldia

fertilizer plants. The Trombay plant will be designed to produce about 3000 te/day of 15:15:15 NPK fertilizer, which will be one of the biggest in the world, while Haldia project will be designed to produce about 1,500 te/day of the same. The advantage is that this process can produce water-soluble phosphatic fertilizer without the use of sulphur.

[*ibid*, 29]

New Fertilizer Projects

Besides the three coal-based plants, FCI is preparing a feasibility report for a fertilizer plant at Paradeep (Orissa). The Indian Farmers' Fertilizer Corporation will set up a fertilizer factory at Kandla in Gujarat costing Rs 90/- crores, which will be commissioned by October 1962.

A fertilizer granulation plant is being set up at Rajpura, about 40 km. from Chandigarh in Punjab and it will go into production in February 1971. Initially it will have a capacity to manufacture 36,000 tonnes of various grades of balanced fertilizer granules. The production will be stepped up to 72,000 tonnes after 6 months.

Another granules plant with a capacity to produce 30,000 tonnes is proposed to be set up at Palamau district by the Bihar State Cooperative Marketing Union.

The Ahmedabad Municipal Corporation, in co-operation with the Gujarat Agro-Industries Corporation, will set up a fertilizer plant in the city at a cost of Rs. 1 crore. It will use city's garbage as the main raw material.

There is also a proposal to set up a fertilizer factory in the cooperative sector in Thana district (Maharashtra). It will produce ammonia, ammonium chemicals and soda ash.

India's first liquid fertilizer plant will go on stream at Chandigarh within 2 years under the auspices of the Punjab Cooperative supply and Marketing Federation. This fertilizer can be used in aerial spraying and it decreases the cost of labour.

[*ibid*]

STATISTICS

TABLE 1—COMMERCIAL FERTILIZER: PRODUCTION AND CONSUMPTION

Continent and Country	Production						Consumption					
	July-June						July-June					
	1967/68	1968/69 ¹	1967/68	1968/69 ¹	1967/68	1968/69 ¹	1967/68	1968/69 ¹	1967/68	1968/69 ¹	1967/68	1968/69 ¹
	Nitrogen (N)	Phosphate (P ₂ O ₅)	Potash (K ₂ O) ²	Nitrogen (N)	Phosphate (P ₂ O ₅)	Potash (K ₂ O) ²	Nitrogen (N)	Phosphate (P ₂ O ₅) ³	Potash (K ₂ O)	Nitrogen (N)	Phosphate (P ₂ O ₅) ²	Potash (K ₂ O)
1	2	3	4	5	6	7	8	9	10	11	12	13
EUROPE												
Austria	252.0	*70.0	—	254.3	*72.3	—	*100.7	*125.0	162.2	*114.5	*120.0	*142.7
Belgium	*350.0	*501.2	—	*400.0	*571.4	—	170.7	*158.9	175.0	170.2	*184.7	175.0
Bulgaria ⁴	353.9	89.2	—	504.0	150.0	—	323.2	260.4	23.4	*370.0	292.0	*40.0
Czechoslovakia	*257.0	*266.1	—	*263.9	*250.2	—	*288.4	*250.5	410.2	*324.0	*282.2	468.0
Denmark ⁷	59.6	85.4	—	62.3	86.9	—	232.6	119.7	173.8	249.1	124.0	180.7
France	*233.0	*1800.0	*1800.0	*1372.0	*1374.0	*1721.0	1133.1	*1505.2	*1158.3	*1210.0	*1587.4	*1172.7
Germany Eastern	4336.0	*304.6	42205.6	4351.4	*345.8	42293.0	445.1	*360.4	592.4	*510.7	*361.0	*650.0
Hungary ⁴	184.7	152.7	—	245.1	155.9	—	236.6	158.0	119.0	304.6	176.2	148.2
Italy	1095.8	552.8	162.2	1088.2	554.1	184.0	479.7	464.5	178.4	514.3	470.0	176.7
Netherlands	849.3	251.3	0.8	954.1	273.3	1.0	343.5	105.7	128.2	339.2	103.9	125.1
Norway	358.8	84.1	—	373.7	87.3	—	67.5	52.7	58.7	70.9	53.8	*59.5
Poland	4593.6	*380.3	—	4758.9	*474.4	—	604.8	*420.8	773.4	706.9	*487.7	897.4
Romania ⁴	372.3	164.7	—	420.7	181.8	—	288.6	135.2	16.9	330.0	140.5	14.1
Spain	424.9	327.5	562.8	494.0	356.5	588.1	477.8	350.5	*136.1	568.2	389.1	*162.3
Sweden ¹¹	139.8	131.4	—	143.8	149.6	—	181.4	128.8	118.7	190.9	139.4	125.8
United Kingdom ¹¹	855.0	429.6	—	911.3	436.8	—	12908.8	13464.3	12500.4	12952.4	12447.0	12484.5
Yugoslavia	101.0	203.7	—	119.8	172.5	—	206.9	177.5	132.0	270.3	159.4	181.6
U.S.S.R. ⁴	*3453.0	1867.0	2868.0	*3750.0	1934.0	3120.0	3089.0	1697.0	2136.0	3454.0	1748.0	2210.0
NORTH AMERICA												
Canada	470.1	488.9	2696.2	*500.0	*510.0	*2990.3	284.6	378.9	254.7	*390.0	*380.0	*230.0
Costa Rica ⁴	*12.0	—	—	*15.0	—	—	*15.7	7.5	8.9	*16.0	*9.0	*15.0
Cuba	*10.0	*9.0	—	*25.0	*3.0	—	*170.0	*99.0	*56.3	*175.0	*113.0	*150.0
Mexico	*173.0	*92.8	—	*196.0	*107.5	—	*298.0	*110.0	*28.0	*345.0	*122.1	*40.0
United States	*176607.0	4992.0	2456.0	*176778.0	4552.0	2486.0	*186157.5	*18,194040.0	*183440.5	*186198.6	*18,194168.8	*183506.8
SOUTH AMERICA												
Argentina	10.7	3.8	—	*24.0	*4.0	—	37.9	20.8	7.6	*31.0	*24.0	*9.0
Brazil ⁴	7.6	92.3	—	9.3	109.4	—	106.4	165.8	137.0	144.2	214.1	184.3
Chile ⁴	104.9	2.9	17.3	116.6	5.1	15.4	12.7	58.3	6.3	24.7	100.7	9.6
Colombia	*40.0	*6.5	—	*47.0	*7.5	—	*47.0	*55.0	*40.0	*53.0	*60.0	*45.0
Peru	*20*28.0	*20*9.0	*21*1.0	*20*25.0	*20*9.0	*21*1.0	*68.0	*10.0	*7.0	*55.0	*11.0	*12.0

TABLE 1 (Contd.)—COMMERCIAL FERTILIZER: PRODUCTION AND CONSUMPTION

Continent and Country	Consumption											
	Production						July-June					
	1967/68			1968/69 ¹			1967/68			1968/69 ¹		
	Nitrogen (N)	Phosphate (P ₂ O ₅)	Potash (K ₂ O) ²	Nitrogen (N)	Phosphate (P ₂ O ₅)	Potash (K ₂ O) ²	Nitrogen (N)	Phosphate (P ₂ O ₅) ³	Potash (K ₂ O)	Nitrogen (N)	Phosphate (P ₂ O ₅) ³	Potash (K ₂ O)
1	2	3	4	5	6	7	8	9	10	11	12	13
ASIA												
China, Taiwan	162.6	37.4	—	194.8	43.2	—	161.2	38.3	57.0	171.0	39.8	61.9
India	*402.6	*207.1	—	*563.0	*213.0	—	*1135.7	*438.2	*205.8	*1222.0	*296.0	*164.0
Indonesia	*41.0	—	—	*47.0	—	—	*105.2	*6.0	*5.5	*198.2	*7.0	*7.0
Iran	*25.4	—	—	*25.7	—	—	*46.0	*28.0	*1.3	*452.0	*30.0	*1.9
Israel	25.9	13.5	330.3	27.6	13.7	344.3	28.3	11.8	6.4	*30.0	12.3	6.6
Japan	2034.7	710.2	—	2107.0	762.8	—	889.4	665.3	652.2	907.0	697.0	696.0
Korea, North	*115.0	*80.0	—	*117.0	*80.0	—	*117.0	*85.0	*10.0	*117.0	*80.0	*54.0
Korea, Rep. of ⁴	150.1	6.3	—	315.3	27.6	—	227.6	132.7	76.2	285.9	121.4	71.2
Pakistan	*107.2	*3.2	—	*135.0	*2.8	—	*253.0	*43.2	*16.0	*319.0	*52.8	*20.0
Philippines	43.5	21.8	—	45.6	36.1	—	64.3	23.8	*30.0	63.4	45.1	*40.0
Thailand ⁴	8.9	—	—	*10.0	—	—	*52.0	35.7	12.7	*50.0	*40.0	*15.0
Turkey ⁴	32.2	35.1	—	34.5	46.5	—	138.1	132.2	8.6	186.6	181.7	11.7
Viet-Nam North	—	*15.0	—	—	*5.0	—	*13.0	*15.0	—	*16.0	*10.0	—
Viet-Nam, Rep. of ⁴	—	—	—	—	—	—	68.7	*31.4	19.1	*60.0	*35.0	*20.0
China, Mainland	*850.0	*360.0	—	*900.0	*390.0	—	*1632.0	*363.0	—	*2160.0	*330.0	—
AFRICA												
Algeria	—	15.2	—	—	17.6	—	14.5	20.1	11.7	13.3	23.9	12.2
Kenya	—	*0.6	—	—	—	—	*13.0	*21.0	*2.8	*15.0	*20.0	*3.0
Morocco ⁴	*2.1	*107.0	—	*1.1	*137.8	—	*36.1	*31.0	*17.4	*38.1	*31.5	*20.0
Rhodesia, Southern	—	*25.5	—	*2.0	*30.0	—	*42.0	*25.5	*17.7	*42.0	*30.0	*20.0
South Africa ⁴	*105.0	*267.1	—	*150.0	*270.8	—	*131.0	*247.0	*86.3	*143.9	*259.2	*96.1
Tunisia ⁴	0.3	182.6	—	0.4	183.2	—	5.5	14.4	3.1	9.2	30.4	3.6
United Arab Rep. ⁴	*125.0	455.0	—	*112.0	*60.0	—	244.5	38.8	1.2	*270.0	*50.0	*1.5
OCEANIA												
Australia	*55.0	960.1	—	*74.0	851.7	—	*147.0	*880.0	*85.0	*160.0	*890.0	*90.0
New Zealand	—	281.3	—	—	323.5	—	4.9	282.1	71.6	7.3	323.6	84.1

¹Preliminary. ²Output of potash fertilizers is in excess of actual performance due to the unidentified double counting of some products used for technical purposes (estimated at 4-5 per cent of the total). ³Excluding ground rock phosphate. ⁴Calendar year referring to the first part of the split year. ⁵Excludes "Other citrate soluble phosphates". ⁶Includes ground rock phosphate. ⁷Fertilizer year: August-July. ⁸Cement dust. ⁹Fertilizer year: May-April. ¹⁰Includes production for technical purposes. ¹¹Fertilizer year: June-May. ¹²Deliveries by manufacturers to first buyers and deliveries of imported fertilizers, whether for straight application or for further processing by other manufacturers into compounds. ¹³Figures cover manufacturers' deliveries to merchants or to farmers, whether in compound form or straight, plus imported fertilizers delivered for direct application. ¹⁴Fertilizer year: April-March. ¹⁵Production of 3,753,000 and 4,177,000 metric tons N, as officially reported for 1967 and 1968 was assumed to include also technical nitrogen. ¹⁶Production for fertilizer purposes only. ¹⁷Excluding sodium nitrate. ¹⁸Includes Puerto Rico. ¹⁹Available P₂O₅. ²⁰Includes guano. ²¹Guano only. ²²Excludes North Korea for which no data are available. ²³Tripolitania only. ²⁴Excludes China (Mainland), for which no data are available.

[Monthly Bull. of Agric. Econ. and Statistics, 19 (2) (1970), 12]

TABLE 2—HIGH YIELDING VARIETY PROGRAMME ACHIEVEMENT 1966-67 TO 1968-69 AND TARGET DURING 1969-70

(Area in '000 acres)

Zone/ State	1966	1966-67	Total	1967	1967-68	Total	1968	1968-69	Total	1969-70	1969-70*	Total
	Kharif	Rabi Summer	1966-67	Kharif	Rabi Summer	1967-68	Kharif	Rabi Summer	1968-69	Kharif	Rabi Summer	
SOUTH	629	942	1,571	1,408	1,369	2,777	2,058	1,475	3,533	3,760	2,405	6,165
Andhra Pradesh	152	648	800	200	860	1,060	374	301	675	1,035	619	1,654
Kerala	80	94	174	132	44	176	113	303	416	200	500	700
Mysore	93	88	181	240	138	378	420	320	740	812	466	1,278
Tamil Nadu	300	108	408	820	315	1,135	1,139	551	1,690	1,669	806	2,475
Pondicherry	4	4	8	16	12	28	12	—	12	44	14	58
WEST	569	534	1,103	1,623	1,642	3,265	3,406	1,375	4,781	6,769	2,333	9,102
Gujarat	61	35	96	381	452	833	523	480	1,003	910	649	1,559
Madhya Pradesh	171	42	213	186	112	298	457	200	657	802	400	1,202
Maharashtra	312	431	743	948	756	1,704	2,164	224	2,388	4,340	574	4,914
Rajasthan	21	23	44	100	310	410	250	471	721	702	700	1,402
Goa	4	3	7	8	12	20	12	—	12	15	10	25
NORTH	356	1,158	1,514	891	5,971	6,861	1,777	9,568	11,345	3,451	9,932	13,383
Haryana	—	32	32	—	250	250	172	640	812	525	642	1,177
Punjab	65	201	266	240	1,579	1,819	187	2,500	2,687	600	3,000	3,600
Jammu & Kashmir	20	2	22	101	70	171	311	90	401	332	100	432
Delhi	1	3	4	9	13	21	16	67	83	29	40	69
Uttar Pradesh	266	197	1,183	536	4,031	4,567	1,071	6,214	7,285	1,860	6,000	7,860
Himachal Pradesh	4	3	7	5	28	33	20	57	77	95	150	245
EAST	264	208	472	928	1,123	2,052	1,291	1,656	2,947	3,317	2,840	6,157
Assam	6	3	9	53	9	63	127	44	171	231	61	292
Bihar	175	71	246	437	824	1,261	551	957	1,508	808	1,275	2,083
Orissa	44	81	125	175	142	317	115	270	385	248	484	732
West Bengal	39	53	92	260	148	408	498	385	883	2,030	1,020	3,050
Tripura	—	—	—	—	—	1	—	—	—	—	—	—
Manipur	—	—	—	2	—	2	—	—	—	—	—	—
ALL-INDIA Achievement	1,818	2,842	4,660	4,850	10,105	14,955	8,532	14,074	22,606	—	—	—
Targets	2,652	4,429	7,081	7,857	10,160	18,017	13,108	14,437	27,545	17,297	17,510	34,887
Achievement as Percentage to Target:	68.6	64.2	65.8	61.7	99.5	83.0	65.1	97.5	82.1	—	—	—

*Target

[FAI Inf. Serv. 11 (5) (1970), 10]

TABLE 3—NAPHTHA REQUIREMENTS OF FERTILIZER AND PETROCHEMICAL INDUSTRIES

Name of Industry	Place	(Figures in thousand tonnes)	
		1970	1971
1. Gorakhpur Fertilizers	Gorakhpur	90	90
2. Indian Explosives Ltd.	Kanpur	110	185
3. Barauni Fertilizers	Barauni	—	44
4. Sindri Fertilizers	Sindri	20	20
5. Rourkela Fertilizers	Rourkela	25	50
6. Durgapur Fertilizers	Durgapur	27	120
7. Gujarat State Fertilizer Corporation	Baroda	170	220
8. D.C.M. Fertilizers	Kota	115	115
9. Trombay Fertilizers (including for Methanol)	Bombay	106	116
10. Union Carbide India Ltd.	Bombay	80	80
11. National Organic Chemicals	Bombay	180	225
12. Hindustan Organic Chemicals	Bombay	1	2
13. F.A.C.T.	Alwaye	60	75
14. Cochin Fertilizers	Cochin	27	120
15. Parry's Fertilizers	Ennore	15	15
16. Madras Fertilizers	Madras	—	150
17. Coromandel Fertilizers	Vishakhapatnam	80	80
Total	India	1105	1707

[Note: On the present level of prices, the total value of naphtha required during 1970 and 1971 will be approximately Rs. 10.5 crores and Rs. 16.2 crores respectively.

On the present level of prices, the total value of naphtha indigenously produced during 1970 will be approximately Rs. 17.9 crores and this will increase to about Rs. 18.1 crores during 1971.

No shortage of naphtha is anticipated during the next two years.]

(Lok Sabha: April 13, 1970)

[Oil Commentary, 7 (16) (1970), 16]

TABLE 4—FERTILIZERS ACTUALLY RECEIVED IN INDIA DURING 1969

Country	N	P	K	C&F value (Rs. crores)
U. S. A.	302,966	69,381	23,548	60.74
Canada	42,903	—	21,800	7.04
Japan	67,220	406	406	9.38
U. K.	28,890	—	—	3.92
West Germany	15,415	520	—	2.42
Belgium	5,302	—	—	0.76
Holland	12,468	—	—	2.02
Austria	4,066	—	—	0.63
Spain	8,864	—	—	1.08
Kuwait	4,761	—	—	0.57
Sweden	10,576	—	—	1.75
Norway	2,439	—	—	0.54
Denmark	1,352	—	—	0.15
U. S. S. R.	41,440	—	—	6.62
Poland	42,355	—	—	5.22
Bulgaria	44,039	—	—	5.68
Rumania	10,680	—	—	1.41
Hungary	22,157	—	—	2.86
Total:	667,893	70,307	45,754	112.79

Note: The above figures do not include import of muriate of potash by S.T.C.

[Sri Annasaheb P. Shinde, Minister of State in the Ministry of Food, Agriculture, Community Development & Cooperation. Statement referred to in reply to Rajya Sabha Starred Question No. 145 for reply on 27th February, 1970]

TABLE 5—IMPORTS OF FERTILIZERS DURING 1968-69 AND 1969-70 (APRIL- MARCH)

	(Tonnes)	
Fertilizer	1968-69	1969-70
Ammonium sulphate (20.6% N)	1,273,808	790,062
Urea (46% N)	1,031,588	937,613
Ammonium sulphate nitrate (26% N)	10,513	—
Calcium ammonium nitrate (16%N)	96,367	83,394
Ammonium chloride (25% N)	46,572	—
Ammonium phosphate (20-20-0)	50,222	—
Diammonium phosphate (18-46-0)	213,200	125,096
Nitrophosphate (20-20-0)	52,931*	6,901
N. P. K. (12-24-12)	6,135	—
„ (14-14-14)	76,238	11,700
„ (14-28-14)	2,000	53,530
„ (15-15-15)	10,495	118,750
Muriate of Potash (60% K ₂ O)	205,787	27,282†
Sulphate of Potash (50% K ₂ O)	—	4,035
	N	846,941
	P ₂ O ₅	132,539
	K ₂ O	185,491
		666,579
		93,363
		45,605†

*Includes different grades.

†Does not include IPSA imports.

[FAI Abstracts, 9 (7) (1970), 10]

TABLE 6—UTILIZATION OF NATURAL GAS IN INDIA

(mil. cu. metres)									
Assam					Gujarat				Grand Total
Year	A.O.C.*	O.I.L.*	Others	Total	Uttran Power House	Dhuwaran Power House	Others	Total	
1961	153.92	13.66	3.28	170.86	—	—	—	—	170.86
1962	165.04	17.08	4.93	187.05	—	—	—	—	187.05
1963	142.81	23.23	6.03	172.07	—	—	—	—	172.07
1964	141.20	30.04	10.13	181.37	—	0.65	—	0.65	182.02
1965	135.46	41.38	10.95	187.79	9.83	127.02	—	136.85	324.64
1966	145.31	64.19	46.09	255.79	65.79	51.21	—	117.00	372.59
1967	139.94	71.40	51.24	262.58	102.08	52.48	48.36	202.92	465.50
1968	146.19	66.03	104.89	317.11	106.55	69.88	110.94	287.37	604.48

*Utilized for field operations.

[Oil Statistics, 7 (3) (1969), 7]

TABLE 7—IMPORTS OF CRUDE OIL AND PETROLEUM PRODUCTS INTO INDIA

(Quantity: Thousand tonnes)

(Value: Rs. lakhs)

Products	1964		1965		1966		1967		1968	
	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value
Light distillates	97.40	278.98	92.07	262.65	63.55	280.82	60.15	256.12	56.89	282.44
Kerosenes	1,326.37	1,992.43	1,421.76	1,851.97	1,155.12	1,846.50	484.37	998.65	418.06	961.34
Diesels	595.11	722.89	662.39	739.69	312.49	422.08	—	—	—	—
Heavy ends	566.36	369.48	433.80	285.37	325.06	269.44	28.20	29.90	54.67	48.18
Bitumen	7.39	17.86	1.11	3.54	—	—	—	—	—	—
Lubricants	363.26	1,995.96	259.09	1,329.67	345.81	2,330.62	378.96	2,616.42	403.04	2,781.74
Others	—	—	—	—	0.14	1.25	—	—	—	—
Total	2,955.89	5,377.60	2,870.21	4,472.89	2,202.17	5,130.71	951.67	3,901.09	932.65	4,073.70
Crude oil	6,791.11	4,259.04	6,810.97	4,037.89	7,457.13	5,610.37	8,703.78	7,959.18	10,449.99	9,387.67
Grand Total	9,747.00	9,636.64	9,681.18	8,510.78	9,659.30	10,741.08	9,655.45	11,860.27	11,382.64	13,461.37

[Oil Statistics, 7 (3) (1969), 9]

TABLE 8—PACKING CONDITIONS FOR FERTILIZER FOR CARRIAGE BY RAIL

I. *Packing conditions P7, P8, P9 and P12

S. No. of packing condition	Maximum net weight of contents	Porter (1) per 37/40 inch (2.349 cm)	Shot (2) per inch (2.54 cm)	Standard size and tare weight of the bags			
				Length in inches (metres)	Width in inches (metres)	Tare weight of the bag	Trade name
P/7	100 kg.	6	8	44" (1.1176)	26½" (0.6731)	2¼ lbs. (1.0205 kg.)	B. Twill
P/8	100 kg.	8	9	40" (1.0160)	28" (0.7112)	2¼ lbs. (1.0205 kg.)	D.W. Heavy Cess
P/9	50 kg.	8	9	28" (0.7112)	25" (0.6350)	1 lb 7 ozs. (0.6520 kg.)	D.W. Heavy Cess
	50 kg.	8	9	27" (0.6858)	20" (0.5080)	18 ozs. (0.5103 kg.)	D.W. Heavy Cess
	50 kg.	8	8	33" (0.8382)	24" (0.6096)	1 lb 9 ozs. (0.7087 kg.)	D.W. Nitrate Bag
	50 kg.	8	9	31" (0.7478)	20" (0.5080)	1 lb 4 ozs. (0.5670 kg.)	D.W. Nitrate
	50 kg.	6	8	36" (0.9144)	22" (0.5588)	1 lb 9 ozs. (0.7087 kg.)	B. Twill
P/12	100 kg.	8	9	44" (1.1176)	26½" (0.6731)	25/8 lbs. (1.1906 kg.)	A. Twill
	100 kg.	8	8	44" (1.1176)	26½" (0.6731)	2½ lbs. (1.1839 kg.)	Liverpool Twill

II. *Packing condition P/28

Must be securely packed in gunny or hessian or in bags

III. *Packing condition P/36

No packing required when in wagonloads, but when tendered in small lots, must be in bundles securely tied or securely packed in gunny or in bags.

IV. *Packing condition IP/3(b)

The outer container must be lined with bitumenised water-proof paper of 130 to 150 grammes per sq. inch polythene or cellulose film or other suitable water-proof material.

(1) Porter—(a) For Hessian No. of warp threads per 37/40 inch (2.349 cm.)

(b) For D.W. (Double warp plain fabrics) number of warp threads per 37/40 inch (2.349 cm.) divided by 2.

(c) For Twills—No. of warp threads per 37/40 inch (2.349 cm.) divided by 3. (Twills are always of double warp).

Warp—The threads length ways in fabric as woven.

The term 'Porter' is used in the measurement of the spacings of warp threads in jute fabrics; the number of porters indicates the closeness (or openness) of the warp.

[Contd.]

- (2) Shot —One weft thread passing from one selvedge to the other. It is the number of weft threads calculated per inch (2.54 cm) of the cloth. Selvedge means the two closed edges of the cloth.
Weft-Threads widthways in a fabric as woven.

Following general precautions are necessary to avoid any qualified remark being passed by the Railways on Railway Receipts:

- (i) The jute bag should not be wet or torn, parched, or re sewn or repaired. The bag should have no holes. The stitches should not be slack or loose. All the loose ends of the threads used for stitching should be securely fastened.
- (ii) There should be adequate empty space left after filling the bag with the contents and then the mouth of the bag should be rolled down and sewn. This does not apply to valved bags which automatically close after machine filling.
- (iii) Jute twine used for sewing must be at least of 3 ply. When bags are machine stitched, stitching may be done with cotton twine.

[*Fertilizer Statistics, 1968-69* (Fert Assn. of India, New Delhi) 1969, 403]

TABLE 9—QUARTERWISE IMPORTS AND DISTRIBUTION OF MURIATE OF POTASH IN INDIA

(58/60% K₂O) 1969-70 (April/March)

(tonnes)

Quarter	Imports through		Distribution through		Total (1969-70) April/March	
	IPSA	Pool	IPSA	Pool	Imports	Distribution
1st Quarter	35,073	—	41,057*	5,630	35,073	46,687
2nd Quarter	27,546	—	42,279	326	27,546	42,605
3rd Quarter	41,840	14,924	70,023	—	56,764	70,023
4th Quarter	20,601	23,528	45,911	—	44,129	45,911
Total:	125,060	38,452	199,270	5,956	163,512	205,226

*In addition, 130 tonnes of Muriate of Potash of grade 48/52% K₂O was distributed during the year.

[*FAI Inf. Serv.*, 9 (12) (1970), 8]

TABLE 10—PRODUCTION OF SINGLE SUPERPHOSPHATE IN INDIA (TONNES)

Year	Capacity	Production	Percentage of Capacity used
1964-65	141,750	121,700	86
1965-66	158,550	109,110	69
1966-67	176,250	120,200	67
1967-68	176,250	147,480	83
1968-69	176,410	109,870	55
1969-70	208,000 (estimated)	102,000 (estimated)	49

[*FAI Inf. Serv.* 11 (9) (1970) 5]

The following papers and short communications have been accepted for publication in the above issue of TECHNOLOGY.

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A method is described for the evaluation of surface area from porosimetry data obtained with a 15,000 psi. Aminco-Winslow porosimeter. The values obtained bear close agreement with surface areas determined by the BET method. The method is ideally suited for quality control work, where evaluation of surface area and pore size distribution is a routine affair. The added advantage is that both surface area and pore size distribution can be obtained from a single run.

Cumulative Surface Areas of Porous Catalysts From Pressure Porosimetry

By S. R. NAIDU, R. M. CURSETJI, D. K. GUPTA,
N. C. GANGULI AND S. P. SEN,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

The degree of porosity and size distribution of pores vary from catalyst to catalyst. In fact, the activity of a catalyst for a given reaction is controlled by the pore size distribution. This is because, the availability of a part or whole of the actual surface area in a catalyst for any diffusion controlled reaction will depend on the pore size distribution and the size of the reactant molecules. In porous catalysts almost the entire surface area is contributed by the pore walls of various sizes of pores. However, it should be clearly understood that pores in the catalyst or any porous solid need not always be cylindrical in shape with circular openings. De Boer¹ in his analysis of gas adsorption-desorption isotherms has concluded that five major types hysteresis loops can be recognized in the case of porous solids. He has shown that each of these isotherms will qualitatively account for the predominant presence of a number of pore-shape groups. He has thus classified fifteen types of pore-shapes.

The present paper describes a method of calculating surface areas of pore walls of porous catalysts by using pressure porosimetry.

Pore size distribution can be calculated by number of methods. Shull² evolved a method of inverting experimental gas adsorption isotherms and then comparing with standard patterns derived from mathematical distributions of Maxwellian or Gaussian type. However, the most standard method for the computation of pore size distribution from nitrogen adsorption isotherms is

that of Barrett, Joyner and Halenda³. Later, Pierce⁴ and other workers have simplified this method. These methods assume the pores to be basically cylindrical with circular cross sections and calculations involve elaborate corrections for the adsorbed film thickness. Innes⁵ developed a method for pore size distribution from low temperature nitrogen adsorption isotherms using a parallel plate model of the pores. It is possible to obtain cumulative surface areas during the course of computation of pore size distribution from low temperature adsorption isotherms but the method is very time-consuming. A special mention may be made of the method of Cranston and Inkley⁶, based on low temperature adsorption isotherms. This method permits computation of cumulative surface areas independent of the BET method. Therefore, for routine determination of pore size distribution in catalysts and other porous solids, the simplest and most direct method is that of mercury pressure porosimetry first introduced by Drake and Ritter⁷.

The method is based on the fact that mercury does not wet solid surface at atmospheric pressures, but is forced into the pores on application of external pressure. The volume intruded can be examined as a function of pressure. The pore-size distribution can then be calculated using Washburn's equation⁸⁻⁹,

$$pr = -2\sigma \cos \theta$$

where p is the pressure, r the pore radius penetrated by mercury, σ the surface tension of the penetrating liquid

and θ the angle of contact between solid and liquid interface. Thus, from a knowledge of mercury volume penetration, pore size distributions are readily obtained.

Earlier workers¹⁰⁻¹¹ have calculated surface areas of solids from pressure porosimetry assuming cylindrical pore shapes. More recently, Rootare and Prenzlow¹² developed a method for the determination of surface areas from standard porosimeter pressure-volume curves without assuming any particular pore geometry. The total area of the sample was related to the work required to force mercury into the pores as PV-work. The surface area (A) was obtained by graphically integrating a porosimeter curve between appropriate limits, viz.

$$A = \frac{0.02253}{m} \int_0^{V_{\max}} P dV,$$

where A is the area in square metres/g; m the mass of the sample and $V_{\max}$ the total volume of mercury intruded at the maximum pressure attainable by the porosimeter. It can be readily seen that the above equation will hold only when

$$V_{\max} \sim V_{p_0},$$

where V_{p_0} is the total pore volume of the sample. Hence, this method seems limited to samples without any pore distribution below 60 Å, which is the narrowest pore penetrated by most commercial porosimeters.

The purpose of the present paper is to show that surface areas comparable to those of BET can be obtained from the pressure porosimeter data without taking resort to the elaborate low temperature adsorption isotherms used in the BET method. An advantage of the method lies in the fact that both surface areas and pore size distributions are obtained from a single run.

Experimental

Six different industrial catalysts, developed in this Division of FCI Ltd., with varying surface areas and pore size distributions were selected.

Sample A—Alumina-based nickel catalyst used in primary steam reformation of naphtha.

Sample B—Low temperature CO-conversion shift catalyst.

Sample C—Desulphurizing zinc oxide catalyst with co-precipitated iron oxide.

Sample D—High temperature CO-conversion shift catalyst.

Sample E—Iron oxide powder cured at 450°C.

Sample F—Spent low temperature CO-conversion shift catalyst.

The pore volumes were determined from the difference of apparent and specific volumes obtained by the displacement of the sample with mercury and helium. Low temperature adsorption-desorption isotherms of four samples were plotted using the Adsorptomat* and pore size distributions were measured with a 15,000 psi. pressure porosimeter*.

Assuming the pores to be cylindrical, the volume contribution ΔV_p by all pores corresponding to a small pressures interval Δp can be computed. If Δp is sufficiently small, ΔV_p may be considered to be the volume of a single cylindrical pore of radius r , where r is the average radius of all pores filled with mercury within the pressure interval.

$$\text{Now, } \Delta V_p = \pi r^2 l \text{ or } l = \Delta V_p / \pi r^2 \quad (1)$$

The area of the curved surface of the average cylinder will be,

$$\Delta S = 2 \pi r l \quad (2)$$

Substituting the value of 'l' from (1) we have,

$$\Delta S = 2 \Delta V_p / r \quad (3)$$

If the pressure increments taken are sufficiently small, so that these computations are made at intervals of 10 or 5 Å, complete distribution can be smoothly scanned and thus $\sum \Delta S$ would give the surface area of the solid under test.

A detailed sample calculation of the method for iron oxide catalyst is given in Table 1. The Table 2 contains the comparative data of surface areas obtained from porosimetry and BET method. The data of mercury volume penetration versus applied pressure obtained from pressure porosimeter were converted to volume-radius curves shown in Fig.1. V_p and corresponding pore radii were selected from these curves. Low temperature adsorption-desorption isotherms are shown in Figs. 2 and 3. Volume-radius curves were converted into

their first derivatives $\left(\frac{dv}{dr} \text{ vs } r \right)$, and are shown in Figs. 4

and 5. Fig. 6 is a plot of the cumulative surface area as a function of pore radius.

Results and Discussion

The results of cumulative surface areas and BET areas given in Table 2 show a remarkable agreement. However, the method of pore size analysis should be critically examined before this can be recommended. From Figs. 4 and 5, it is obvious that the smallest pores penetrated by mer-

*Manufactured by American Instrument Co. Silver Spring, Maryland, USA.

TABLE 1—DETAILS OF SAMPLE-CALCULATION

[Wt. of Sample taken = 0.1630 g.]

Pore Radius, Å	Pore Volume, c.c.	ΔV_p , c.c.	Average Pore Radius, Å	Length of Pore $\times 10^{15}$, Å	Δ S. Area of Curved Surface, m^2	Cumulative Surface Area, m^2
500	0.1177	—	—	—	—	—
400	0.1193	0.0016	450	2.51	0.0710	—
300	0.1227	0.0034	350	8.84	0.194	0.265
250	0.1262	0.0035	275	14.73	0.254	0.519
200	0.1293	0.0031	225	19.50	0.275	0.794
190	0.1310	0.0017	195	14.23	0.174	0.968
180	0.1322	0.0012	185	11.16	0.129	1.097
170	0.1340	0.0018	175	18.71	0.205	1.302
160	0.1362	0.0022	165	25.73	0.266	1.568
150	0.1385	0.0023	155	30.48	0.296	1.864
140	0.1410	0.0025	145	37.86	0.345	2.209
130	0.1440	0.0030	135	52.42	0.444	2.653
120	0.1460	0.0020	125	40.76	0.320	2.973
110	0.1490	0.0030	115	72.24	0.521	3.494
100	0.1526	0.0036	105	103.90	0.723	4.217
95	0.1540	0.0014	97.5	46.90	0.287	4.504
90	0.1555	0.0015	92.5	55.83	0.324	4.828
85	0.1560	0.0005	87.5	20.79	0.114	4.942
80	0.1562	0.0002	82.5	9.35	0.048	4.990
75	0.1575	0.0013	77.5	68.93	0.335	5.325
70	0.1580	0.0005	72.5	30.29	0.137	5.462
65	0.1590	0.0010	67.5	69.90	0.296	5.758
60	0.1597	0.0007	62.5	57.07	0.224	5.982
4	0.1597	Nil	—	—	—	—

TABLE 2—COMPARISON OF CALCULATED RESULTS AND STANDARD BET VALUES

Sample	Total Pore Volume, c.c./g.	Pore Volume below 60Å, %	Average Pore Radius, Å	Cumulative Surface Area from Porosi- metry, $m^2/g.$	BET Surface Area, $m^2/g.$
A	0.1884	31.63	73.7	51.89	51.10
B	0.1876	Nil	100.9	42.67	37.16
C	0.1933	17.02	55.7	74.58	69.40
D	0.1802	12.98	83.5	37.10	43.13
E	0.9797	Nil	596.0	36.69	34.43
F	0.2136	18.55	140.0	35.00	30.50

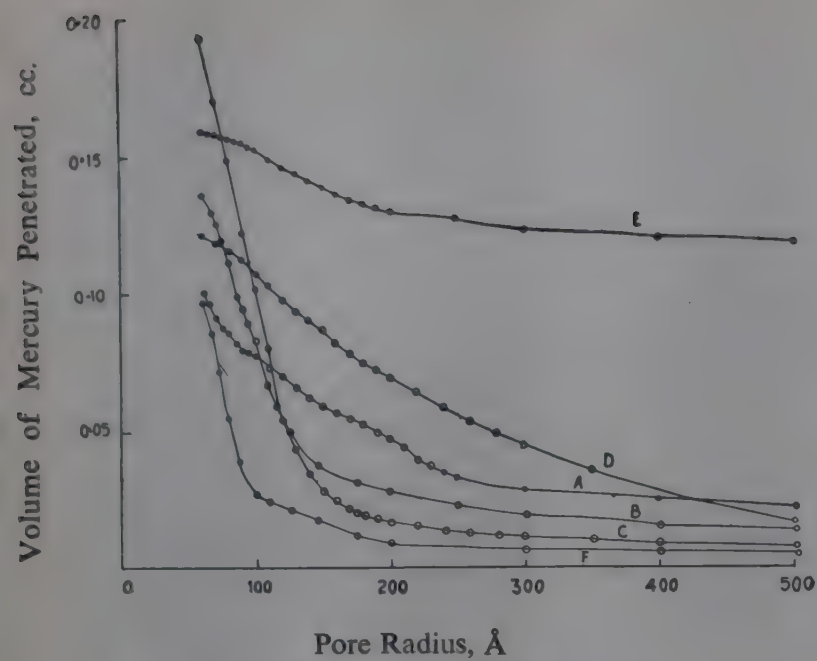


Fig. 1—Penetration Volume-Radius Curves

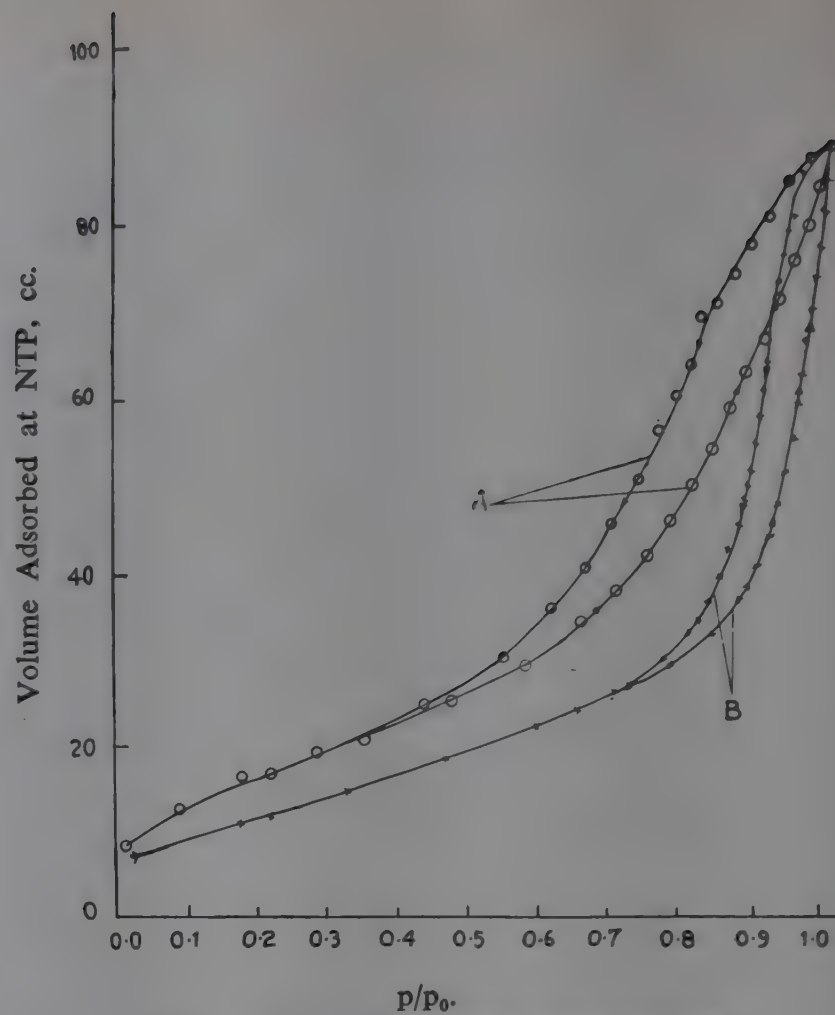


Fig. 2—Low Temperature Nitrogen Isotherms

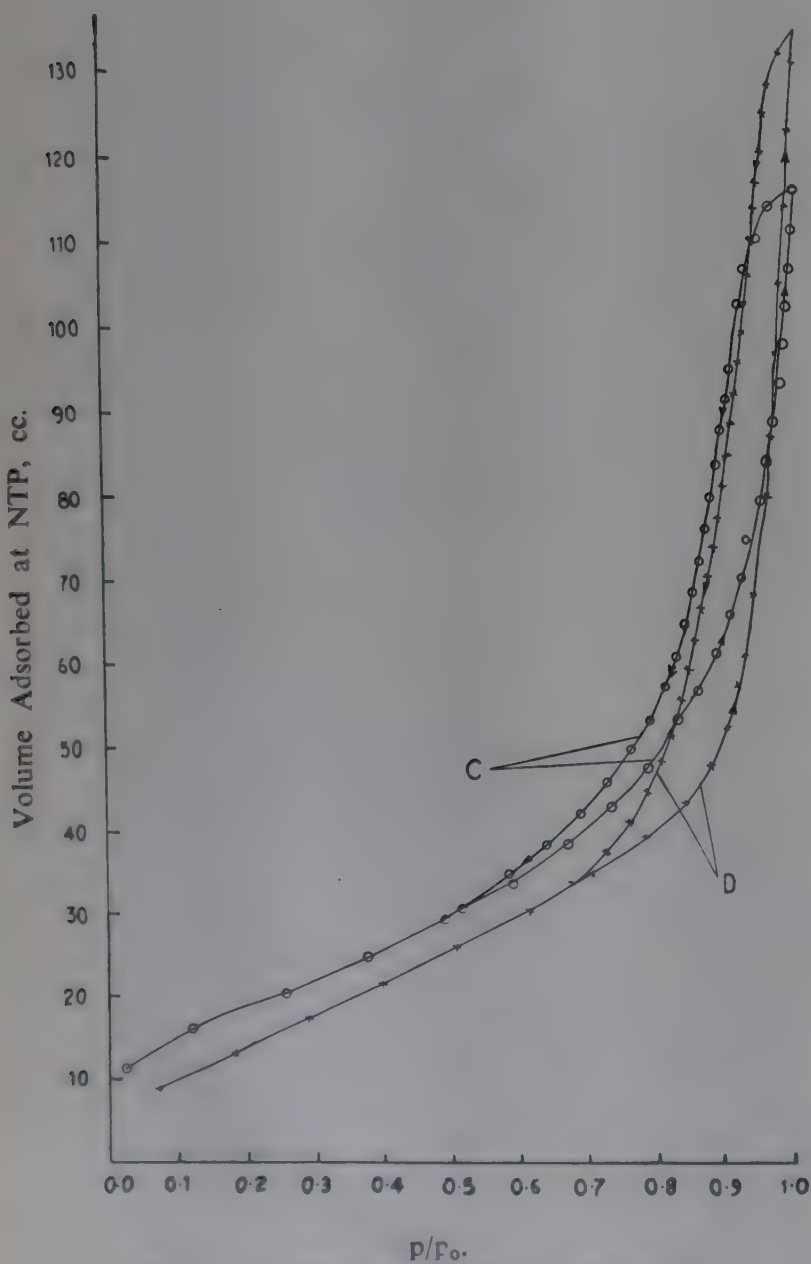


Fig. 3—Low Temperature Nitrogen Isotherms

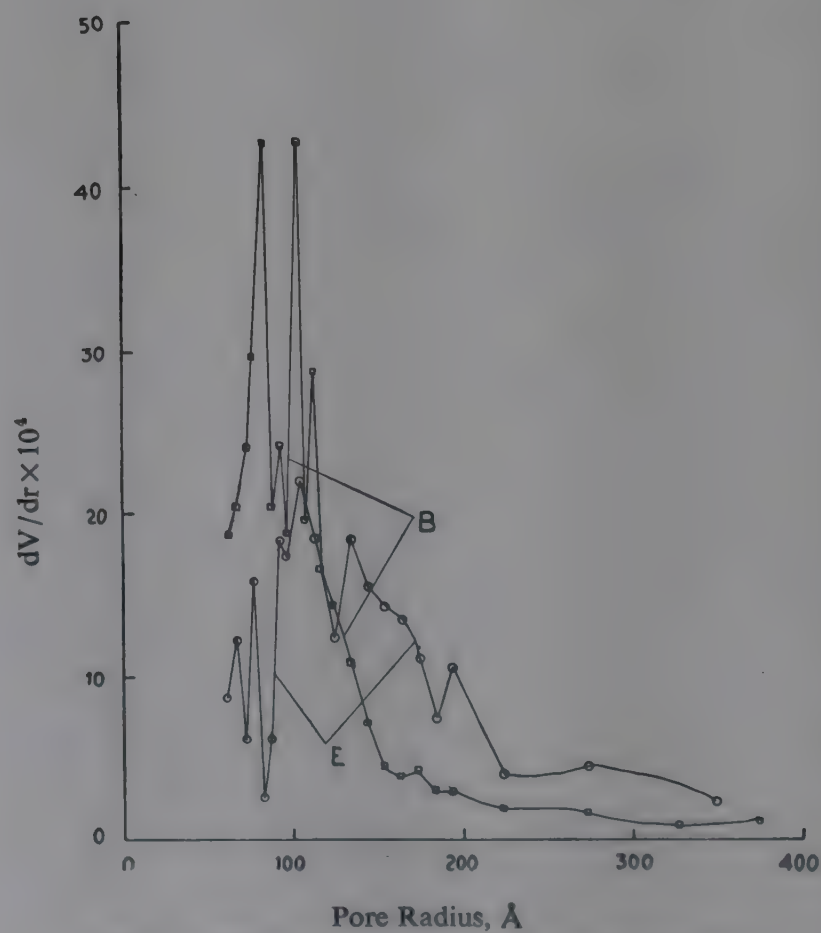


Fig. 4—Differential Curve of Pore Size Distribution

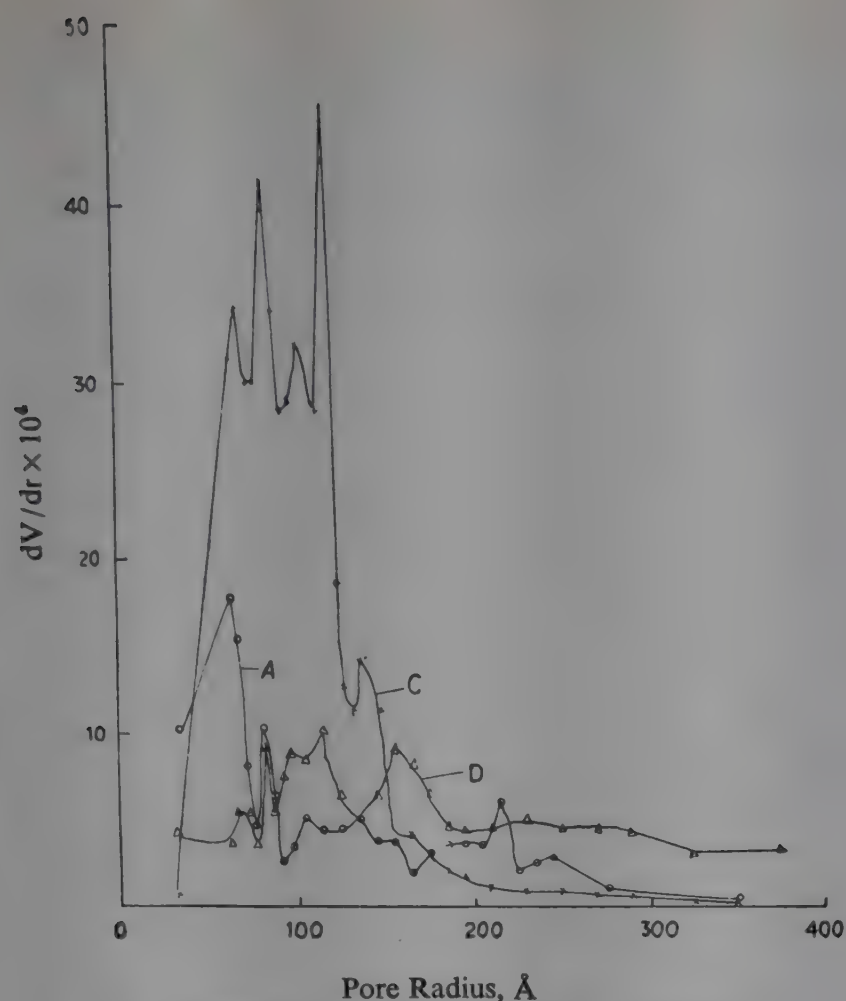


Fig. 5—Differential Curves of Pore Size Distribution

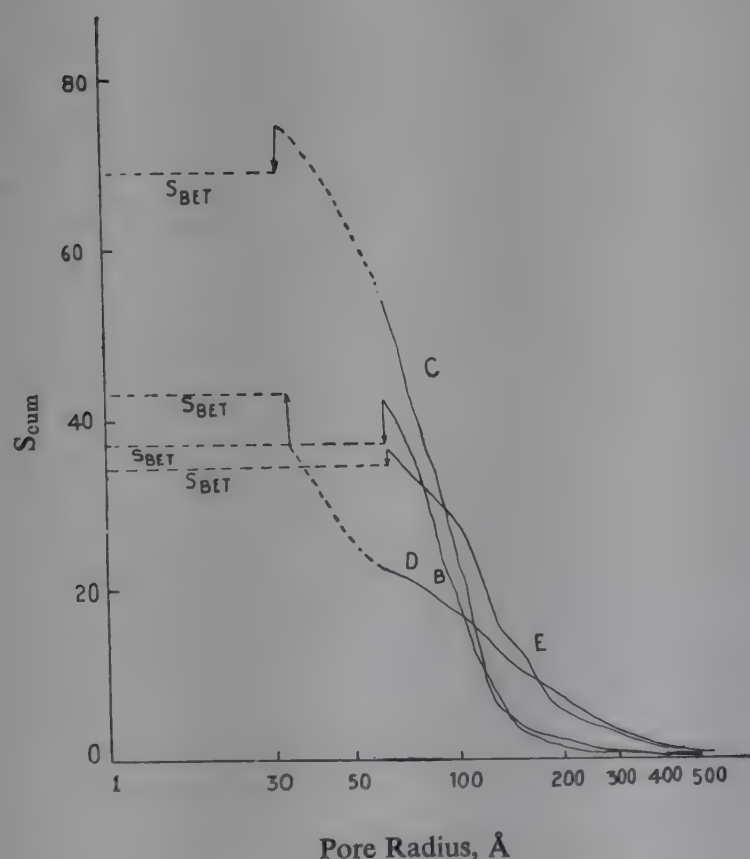


Fig. 6—Cumulative Surface Areas

cury were of the order of 60Å in radius, this being the pore size filled with mercury at the maximum pressure attainable with a 15,000 psi. porosimeter. This means that the pore volume in the sample below 60Å must either be

negligible or must have more or less uniform pore size distribution to justify taking an average radius between 4 and 60Å in order to compute the area contribution by the pores in these regions. From Table 2, it is obvious that samples B and E have no pores below 60Å, while samples C, D and F have only 17.02, 12.98 and 18.55 per cent of pore volume below 60Å. Sample A shows 31.63 per cent of pore volume below 60Å. This sample (A) shows a broad distribution of pores between 400 and 60Å (Fig. 4), indicating that this pattern could probably extended to the lower region also. This assumption seems to be justified by the fact that by averaging pore volume in the lower region between 60 and 4Å, a close agreement has been observed between calculated surface area and BET area.

Pore size distribution is generally classified into macro- and micro-pore regions—all pores below 100Å radius being considered micro-pores**. In most catalysts and other porous solids with highly developed surface areas, a large percentage of the surface area is contributed by pores in the micro-pore region. However, for greater accuracy in the computation of surface areas, pores of upto 400Å radius have been included in our calculation. Furthermore, the surface areas contributed by the pores above 400Å have been found to be negligible, particularly in cases where total surface areas are large.

It seems worthwhile to consider the basic assumptions involved in the theory of pressure porosimetry. Although pressure porosimetry is the most direct method for pore size calculations, it is liable to fail in cases where pores are non-cylindrical as in the case of clay minerals. Ritter and Drake⁷ have recognized the fact that when pores fail to have circular cross-sections, the distribution patterns will change, as constant $2/r$ in Washburn's relation will change. However, they maintain that the distribution curve itself will not change appreciably. It seems likely, therefore, that cumulative surface area also will not deviate greatly from BET area. However, it was considered necessary to examine the nature of the shape of pores in these catalyst samples. Low temperature nitrogen adsorption and desorption isotherms were plotted and the hysteresis loops examined. All these samples have steep hysteresis loops, which have been shown by DeBoer¹ as being caused by cylindrical pores

**Micro-pores are generally regarded as those which contribute most of the surface area in a porous solid—namely pores below 100Å radii. Recently, however, Brunauer (J. Colloid Interface Science. 26, 1968, 45) has defined micro-pores as those in which capillary condensation does not occur, i.e. pores less than 16Å in width.

with circular cross-section. These isotherms also indicate that all the catalysts have a pore size distribution in the higher pore radius region above 100Å, which is confirmed from differential plots.

DeBoer¹ has also shown that if the capillaries are truly cylindrical in shape, $S_{\text{BET}} \sim S_{\text{CUM}}$, where S_{CUM} is the cumulative surface area obtained from the desorption branch of low temperature nitrogen isotherm using the BJH³ method. This seems to apply to pressure porosimetry also particularly in case of sample A, where it is found that the S_{BET} is nearly equal to S_{CUM} . He has shown that when S_{BET} is less than S_{CUM} , the tubular pores may be having closed ends forming an assembly of pores intersecting each other, creating a certain amount of capillary space without a corresponding BET surface. This may explain the slightly higher cumulative surface areas in the case of samples B, C and E. It may be noted that a close agreement between cumulative and BET areas would depend on the correct selection of pore radius intervals. This can be done by a close inspection of the volume-radius curves shown in Fig. 1.

The method described is simple and ideally suited for a rapid and comparative study of surface areas. However, a word of caution may be added here while taking the average of pore radius between 4Å and the smallest pore that can be penetrated by a given porosimeter. If major portion of the surface area is contributed by the pores in this unscanned region, the results will deviate from the BET values. On the other hand, data obtained on a porosimeter covering the entire pore-spectrum

down to the smallest pore, may safely be adapted for the evaluation of surface areas as described in the present paper. DeBoer¹ and other workers⁶ have shown in detail that the non-ideal shape of the pores has a strong bearing on the difference between cumulative and BET surface area values and that these differences may be used to predict a possible predominance of a particular shape. This analysis applies to both isotherm methods as well as pressure porosimetry.

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Studies on structural parameters, like compressive strength, specific pore volume and specific surface area, have been carried out with six carriers composed of different proportions of α and γ -forms of alumina and also with the catalyst made by impregnating these carriers with nickel. The pore size distribution of the six catalyst samples have also been determined. All those results show favourable change in structural properties with increasing proportion of γ -alumina in the carrier.

Effect of *Gamma*-Alumina in Naphtha Reformation Catalyst: Studies on Structural Parameters

By J. MISRA, D. K. MUKHERJEE AND S. P. SEN,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

The activity of suitable refractory-supported nickel catalysts for steam-reforming of hydrocarbons has been studied by many authors¹⁻⁹. Such catalysts in various formulations have been widely employed for commercial use. The most commonly used carrier material for these catalysts is alumina which is highly refractory and can offer stable surface for the active component.

A number of investigations and patents have been referred in the literature, in which hydrocarbon steam-reforming catalysts were prepared by coprecipitation of nickel and aluminium from solutions of their salts¹⁰⁻¹⁶. Catalysts prepared by this method, although quite active^{12, 17 & 18} were found to be very sensitive to carbon deposition resulting in disintegration and dusting¹⁹. The coprecipitated Ni-Al₂O₃ catalysts have appreciable amounts of γ - form of alumina, which is believed to have a large number of acid sites (Lewis) measured by many workers^{20, 21}. The presence of acid sites is responsible for carbon deposition according to the mechanism discussed by Applebey *et al*²².

Attempts were made to neutralize acid sites of such a catalyst by incorporating some basic components like alkali metal oxides⁸. Although the problem of carbon liberation at an economic steam/carbon ratio with such a catalyst could be avoided to some extent yet the activity is reported to be less with an alkalized catalyst^{2, 23}. In addition, the problem of loss of alkali from the catalyst during run is also reported²³. It is also observed that presence of the major amount of γ -alumina in catalyst

makes the structure of the catalyst unstable due to phase transformation from γ to α -form which is accompanied by shrinkage of pores and surface area. The rate of transformation of γ -alumina to α -form depends on temperature, pressure and steam concentration and under the usual conditions of reformation reaction a finite rate is observed²⁴. This structural shrinkage when it takes place to a considerable extent may result in loss of both activity and mechanical strength.

Because of all these problems with γ -alumina, α -alumina which is stable up to 1500°C and possesses much less acid sites is preferred as a carrier-material for the reformation catalyst. Catalysts prepared by impregnating ignited alumina (corundum), consisting mainly of α -form, with nickel are believed to have a better stability.

The structures of both γ - and α -forms of alumina have been discussed in details by Wells²⁵ from which it is observed that while α -alumina has a crystalline structure with hexagonal close-packed lattice, γ -alumina possesses defect spinel structure with cubic lattice having some vacant metal holes in it^{26, 27}. It is probably due to its defect structure that is responsible for a higher surface activity of γ -alumina¹⁷ than that of α -alumina.

So, it is probable to achieve a compromise between activity and stability by incorporating both α - and γ -forms of alumina in the carrier in suitable proportions. With this end in view, investigations have been taken up by the present authors to study the effects of presence of both α - and γ -forms in the carrier of steam-naphtha reformation catalyst. The present work deals with the

studies on structural parameters of a number of carriers and catalysts made therefrom, containing γ -alumina to different extents in addition to α -form. Studies on activity and stability with these catalysts are in progress and will be communicated later.

Experimental and Results

For the purpose of investigations, altogether six samples of alumina-carrier were prepared by varying the proportions of ignited alumina (α -form) and alumina obtained from its basic carbonate by heating upto 850° (Table 1). For preparation of the samples intimate mixtures of finely powdered ignited alumina and precipitated aluminium basic carbonate in different proportions were heated upto 500°C, made into solid cylindrical tablets (8 mm $\times$ 8 mm) and finally cured at 850°C.

The sample A₆ was prepared without using any calcined alumina i.e. 100 per cent of alumina is from precipitated basic carbonate. A portion of each of the six carrier samples prepared as above was impregnated with nickel nitrate and heated at 500°C to decompose the nitrate into oxide. Nickel was incorporated to the extent of approximately 10 per cent by weight in each of the samples. Thus, corresponding the six carrier samples six catalyst samples were prepared as shown in Table 1.

TABLE 1—CHEMICAL COMPOSITION OF CATALYST SAMPLES

Carrier Sample No.	Alumina from Precipitated Basic Carbonate, %	Ignited Alumina (α -Form), %	Catalyst Sample No.	% Ni
A ₁	5	95	NA ₁	9.2
A ₂	10	90	NA ₂	9.8
A ₃	20	80	NA ₃	9.9
A ₄	40	60	NA ₄	9.1
A ₅	70	30	NA ₅	9.7
A ₆	100	0	NA ₆	9.0

X-ray investigations were carried out with each of the alumina-carrier, which show that the six carrier samples contain both α - and γ -forms of alumina but the extent of γ -alumina present in any sample increases with the increase of alumina content obtained from basic carbonate. Thus, γ -alumina is minimum in sample A₁ and maximum in A₆.

Compressive strength, specific pore volume and specific surface area of all the six samples of alumina-carrier as well as those of the catalyst samples have been measured. In addition, the pore size distributions of the catalyst samples have also been determined. Experi-

mental methods adopted for measuring these structural parameters of different samples are described below:

(i) *Compressive Strength*: Compressive strength measurements were carried out by using a tensometer. The load was always applied on the two flat faces of the solid cylindrical pellet under test till it crushed and this crushing load was noted.

(ii) *Specific Pore Volume*: Total pore volume (cc/g.) of all the carrier and catalyst samples was determined from the difference of mercury displacement and helium displacement values. The mercury displacement values were measured by the method described by Juhola and Wiig²⁸ and helium displacement values were determined by helium densitometer.

(iii) *Specific Surface Area*: Surface area in terms of m²/g. was determined with the help of nitrogen adsorption isotherms at liquid nitrogen temperature and applying the BET equation.

(iv) *Pore Size Distributions*: Pore size distributions of the different catalyst samples were determined by using a mercury porosimeter which is based on the principle that the penetration of mercury into the pores of any diameter will depend on the pressure applied according to the following relationship--:

$$D = \frac{4\sigma \cos\theta}{P}$$

where D indicates pore diam., σ is surface tension of mercury, P pressure and θ contact angle of the mercury with the capillary wall. Total volume of pores upto a particular diameter will be equal to volume of mercury penetrated inside the pores upto that diameter. The values of specific pore volume were used to calculate the percentages upto different pore sizes.

The results of all these measurements with the carrier samples are shown in Table 2 while those with the catalyst samples are shown in Table 3.

TABLE 2—STRUCTURAL PARAMETERS OF CARRIER SAMPLES

Sample No.	Compressive Strength, kg/cm ²	Specific Pore Volume, cc/g.	Specific Surface Area, m ² /g.
A ₁	57.7	0.5526	34.07
A ₂	76.0	0.5609	36.40
A ₃	156.5	0.6408	54.90
A ₄	297.3	0.7787	63.40
A ₅	365.3	1.0133	91.03
A ₆	582.0	1.4045	99.70

TABLE 3—STRUCTURAL PARAMETERS OF CATALYST SAMPLES

Sample No.	Compressive Strength, Kg/Cm ²	Specific Surface Area, m ² /g.	Specific Pore Volume, cc/g.	Pore Size Distributions, Å				
				4-175	175-300	300-400	400-500	500-75000
NA ₁	129.2	32.4	0.5188	18.4	10.4	4.7	2.8	63.7
NA ₂	208.7	33.3	0.5200	18.4	9.8	4.9	3.2	63.7
NA ₃	449.3	48.3	0.5320	27.3	6.1	2.3	1.8	62.5
NA ₄	664.0	57.2	0.6219	33.0	3.8	1.4	1.4	60.4
NA ₅	763.5	85.2	0.6731	37.1	3.3	2.6	1.1	56.9
NA ₆	946.3	88.8	0.6851	42.8	1.5	0.3	0.5	54.9

Discussion and Conclusions

The results (Table 2) clearly show that the structural parameters, like crushing strength, pore volume and surface area, increase consistently from samples A₁ to A₆, i.e. with increasing concentration of γ -alumina in the carrier. Higher crushing strength, porosity and surface area of γ -alumina have also been reported by many authors²⁹⁻³¹.

Again, from Table 3, it is observed that compressive strength, specific pore volume and specific surface area of the corresponding catalyst samples also increase steadily with increasing concentrations of γ -alumina. The percentage of pores in the smallest range, viz. between 4 and 175 Å, increases with the γ -alumina concentration of the samples while the same in the higher range, viz. between 500 and 75000 Å decreases in the same direction.

All these changes in the structural parameters with increasing proportion of γ -alumina are favourable for a catalyst. This leads to the conclusion that increase in concentration of γ -alumina in the carrier is favourable for a reformation catalyst so far as its structural parameters are concerned.

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The process of ammonia decomposition on nine different contact materials has been studied in the temperature range 600-750°C. The reaction rate has been found to depend on the catalytic factor in the lower temperature region, while at higher temperatures the rate is controlled by thermal factors. The promoted magnetic oxide of iron is found to be most suitable for industrial application.

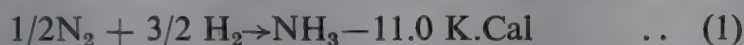
Catalytic Decomposition of Ammonia

By D. K. MUKHERJEE, N. RAY, S. K. SINGH, B. ACHARI
AND S. P. SEN,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Binar*

Introduction

Catalytic decomposition of ammonia has been a subject of interest since the early part of this century, primarily for evaluating the mechanism and kinetics of catalytic synthesis of ammonia. The reaction between nitrogen and hydrogen is reversible and exothermic.



The above reaction proceeds with measurable rate only at very high pressure, thereby making the kinetic studies on ammonia synthesis from nitrogen and hydrogen difficult. So, as a matter of convenience, the decomposition reaction has been studied by many authors, both in static and in flow systems, at atmospheric pressure. The studies in static system could not find any application due to inconsistent results, whereas most of the results of studies in flow system¹⁻⁸ could be applied in deducing workable rate equations. The most successful rate equation is due to Temkin and Pyzhev⁶, which in its simplest form is presented as

$$-\frac{dp_{\text{NH}_3}}{dt} = \frac{K_2 \cdot p_{\text{NH}_3}}{p_{\text{H}_2}^{1.5}} \quad \dots (2)$$

where p_{NH_3} , p_{H_2} are the partial pressure of NH_3 and H_2 respectively and K_2 is the rate constant.

The studies on catalytic decomposition of ammonia could be used for indirect application in evaluating mechanism and kinetics of ammonia synthesis which in turn could be successfully utilized to design ammonia converter. In recent years catalytic decomposition of ammonia as a process has also found direct application^{9,10} in certain industries where the working temperature is well above 500°C. But most of the earlier studies

on ammonia decomposition were carried out at temperatures below 500°C, and as such the rate equations so deduced are not valid for ammonia decomposition process adopted in industries.

One of the most common applications of ammonia decomposition is in modern ammonia plants. Ammonia on complete decomposition will give a mixture of hydrogen and nitrogen, which can be directly used for reduction of catalysts during start-up of a plant. Again, after burning off the hydrogen with controlled quantity of air, the residual nitrogen can be used as an inert gas for flushing various pipelines and equipments and to maintain inert atmosphere.

In practice, ammonia from pressure vessels is cracked to hydrogen and nitrogen in presence of a catalyst. It is essential that the ammonia content of the cracked gas is only in traces. If the ammonia cracked gas contains appreciable quantity of undecomposed ammonia, it has to be removed. But elaborate arrangements for removal of ammonia can be avoided if the decomposition is carried out to such an extent that the ammonia content will be negligible. This can be achieved either by thermal cracking at higher temperatures or by catalytic cracking at moderate temperatures. Operation at high temperature on a commercial scale is uneconomic. If the decomposition process is carried out in presence of a catalyst, the reaction can be made to proceed appreciably close to equilibrium with sufficient rate even at moderate temperatures in the region of 600°C. Thus, catalytic ammonia decomposition process can be advantageously employed on a commercial scale using an efficient catalyst. Several types of catalysts, like nickel on alu-

mina, promoted iron oxide and platinum, are being commercially employed for this purpose.

The present work deals with the studies of ammonia decomposition at various temperatures in the range 600° to 750°C on different types of contact materials to investigate the influence of catalytic and thermal factors on its rate.

Experimental

Description of the Apparatus: A simplified flow diagram of the apparatus used for this investigation is given in Fig. 1. Ammonia is drawn from cylinder (C) and

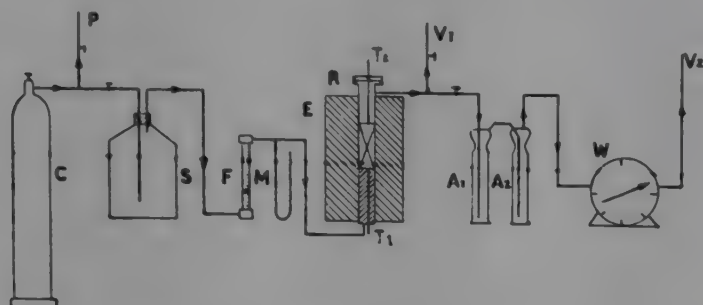


Fig. 1—Flow Diagram of Ammonia Decomposition Unit

after passing it through a surge vessel (S), is allowed to pass through a rotameter (F), to regulate its flow. The reactor (R) consists of a stainless steel tube of 31 mm i.d. and 500 mm length inserted in a vertical tubular electric furnace (E) 50 mm i.d. × 500 mm long. The reactor tube is flanged at the top having a side outlet at about 50 mm from the flanged end. The reactor is packed at the bottom with 200 mm thick layer of inert material acting as preheat zone followed by 125 mm thick layer of catalyst bed. The temperature of the catalyst bed is controlled by an automatic temperature-controller. The temperature of the gas entering the catalyst bed is indicated by a thermocouple (T_1). A similar thermocouple (T_2) indicates the temperature of the gas leaving the catalyst bed.

The metered ammonia gas enters the bottom of the reactor, passes through the preheat zone and the catalyst bed maintained at constant temperature and finally leaves the reactor at the top outlet. To start with a particular catalyst, ammonia is passed for 4 hours to attain a steady state. Under steady conditions of temperature and flow, the cracked gas is passed through a series of two absorbers (A_1 , A_2) containing a known volume of standard sulphuric acid, which will absorb the residual ammonia from the cracked gas. The cracked gas from the absorbers is metered by a wet gas meter (W) and then vented through V_2 . The ammonia leakage of the cracked gas is thus estimated from the volume of acid

consumed by a known quantity of gas. When the estimation of ammonia in the cracked gas is not carried out, it is directly vented after the reactor through V_1 .

Procedure: For the purpose of comparison of activity, several materials of widely different nature were chosen as catalysts, some of which are unconventional for the ammonia decomposition. The samples were classified in three groups—group I consisting of a sample of spherical iron ball and a sample of calcined alumina in the form of extruded rod, group II consisting of four samples of alumina-supported nickel catalysts and group III comprising three iron catalysts. The details including BET surface area of the reduced samples (except samples 1 and 2) are also given (Table 1).

100 c.c. of each of these catalysts were charged in turn in the reactor and tested for their activities at seven different temperatures from 600 to 750°C at intervals of 25°C. These temperature conditions were maintained at the top of the catalyst bed (shown by T_2 in Fig. 1). The temperature (T_1) at the bottom of the catalyst bed indicated the preheat temperature and was always less than the top temperature. The pressure, in all cases, was maintained atmospheric and the space velocity on the basis of inlet ammonia gas was kept constant at 500 (vols. of ammonia gas at N.T.P./Vol.cat./hr.).

Results

The results obtained in terms of concentration of ammonia in the exit gas with all the catalyst samples at different temperatures of reaction and the equilibrium ammonia concentrations at different temperatures are presented in Table 2.

If the partial pressure of ammonia in the exit gas at any particular temperature and the equilibrium partial pressure of ammonia at that temperature are indicated by p_{NH_3} and $p_{\text{NH}_3\text{eq}}$ respectively, the ratio $p_{\text{NH}_3\text{eq}}/p_{\text{NH}_3}$ will be a measure of equilibrium approach. The values of $(p_{\text{NH}_3\text{eq}}/p_{\text{NH}_3}) \cdot 10^4$ corresponding to all the temperatures of experiment with different catalyst samples have been calculated and shown in Table 3. The values of $\log \left(\frac{p_{\text{NH}_3\text{eq}} \times 10^4}{p_{\text{NH}_3}} \right)$ against temperature

have been plotted in Fig. 2. The number indicated against each curve corresponds to the catalyst sample number and line E to equilibrium.

Discussion and Conclusions

From the results, it is observed that of the 9 different catalysts used in the experiment, promoted magnetic oxide of iron (sample 9) shows maximum activity at all

TABLE 1—DETAILS OF THE CATALYST SAMPLES

Group	Catalyst Sample No.	Description	Size & Shape	Composition	Specific Surface Area,* m ² /g.
I	1	Iron balls	Solid balls 8-10 mm diam.	Mainly metallic Iron	1.05 × 10 ⁻⁵
	2	Porous calcined alumina	10 mm. diam × 20 mm. long extruded rods	Mainly Al ₂ O ₃	40.2
II	3	Nickel oxide impreg- nated on porous alu- mina carrier	-do-	Nickel 2.5% Al ₂ O ₃ Rest	10.1
	4	-do-	-do-	Nickel 5.0% Al ₂ O ₃ Rest	9.8
	5	-do-	-do-	Nickel 10.5% Al ₂ O ₃ Rest	10.0
	6	-do-	-do-	Nickel 20.0% Al ₂ O ₃ Rest	9.7
III	7	Iron oxide impregnated on porous alumina carrier	-do-	Iron 3.5% Al ₂ O ₃ Rest	10.6
	8	-do-	-do-	Iron 6.0% Al ₂ O ₃ Rest	10.3
	9	Fused magnetic oxide of iron-promoted with Al ₂ O ₃ and K ₂ O	6-10 mm grits	Al ₂ O ₃ 1.2% K ₂ O 1.2% Fe ₃ O ₄ Rest	9.3

*Specific surface area was determined by the B.E.T. method except in the case of sample 1

TABLE 2—AMMONIA LEAKAGE AT DIFFERENT TEMPERATURES

Sample No.	Temperature, °C						
	600	625	650	675	700	725	750
1	33.33%	17.16%	9.95%	3.68%	0.75%	0.11%	618 ppm
2	39.08%	29.53 "	17.65 "	—	4.17 "	—	0.38%
3	8.58 "	2.72 "	0.75 "	0.21%	0.10 "	368 ppm	280 ppm
4	1.64 "	0.26 "	800 ppm	440 ppm	262 ppm	216 "	180 "
5	0.73 "	0.21 "	638 "	344 "	255 "	201 "	167 "
6	0.68 "	0.19 "	992 "	674 "	282 "	223 "	184 "
7	6.47 "	1.88 "	0.20%	774 "	284 "	220 "	178 "
8	5.00 "	0.92 "	950 ppm	348 "	253 "	206 "	166 "
9	520 ppm	400 ppm	329 "	273 "	228 "	190 "	162 "
Equilibrium Leakage	478 "	388 "	320 "	266 "	222 "	186 "	159 "

TABLE 3—VALUES OF $(\text{pNH}_{3\text{eq.}}/\text{pNH}_3)10^4$ AT DIFFERENT TEMPERATURES

Sample No.	Temperature, °C						
	600	625	650	675	700	725	750
1	12.54	22.61	32.17	72.46	295.86	1694.9	2564.1
2	12.23	13.14	18.13	—	53.19	—	416.67
3	55.70	142.65	427.35	1265.8	2222.2	5050.5	5681.8
4	291.55	1492.5	4000.0	6060.6	8474.6	8620.7	8849.6
5	653.59	1851.9	5000.0	7692.3	8695.7	9259.3	9523.8
6	704.23	2040.8	3225.8	4000.0	7874.0	8333.3	8620.7
7	74.07	2061.9	1600.0	3436.4	7812.5	8474.6	8928.6
8	96.15	421.94	3367.0	7633.6	8771.9	9009.0	9615.4
9	9174.3	9708.7	9737.3	9746.8	9756.3	9775.4	9775.4

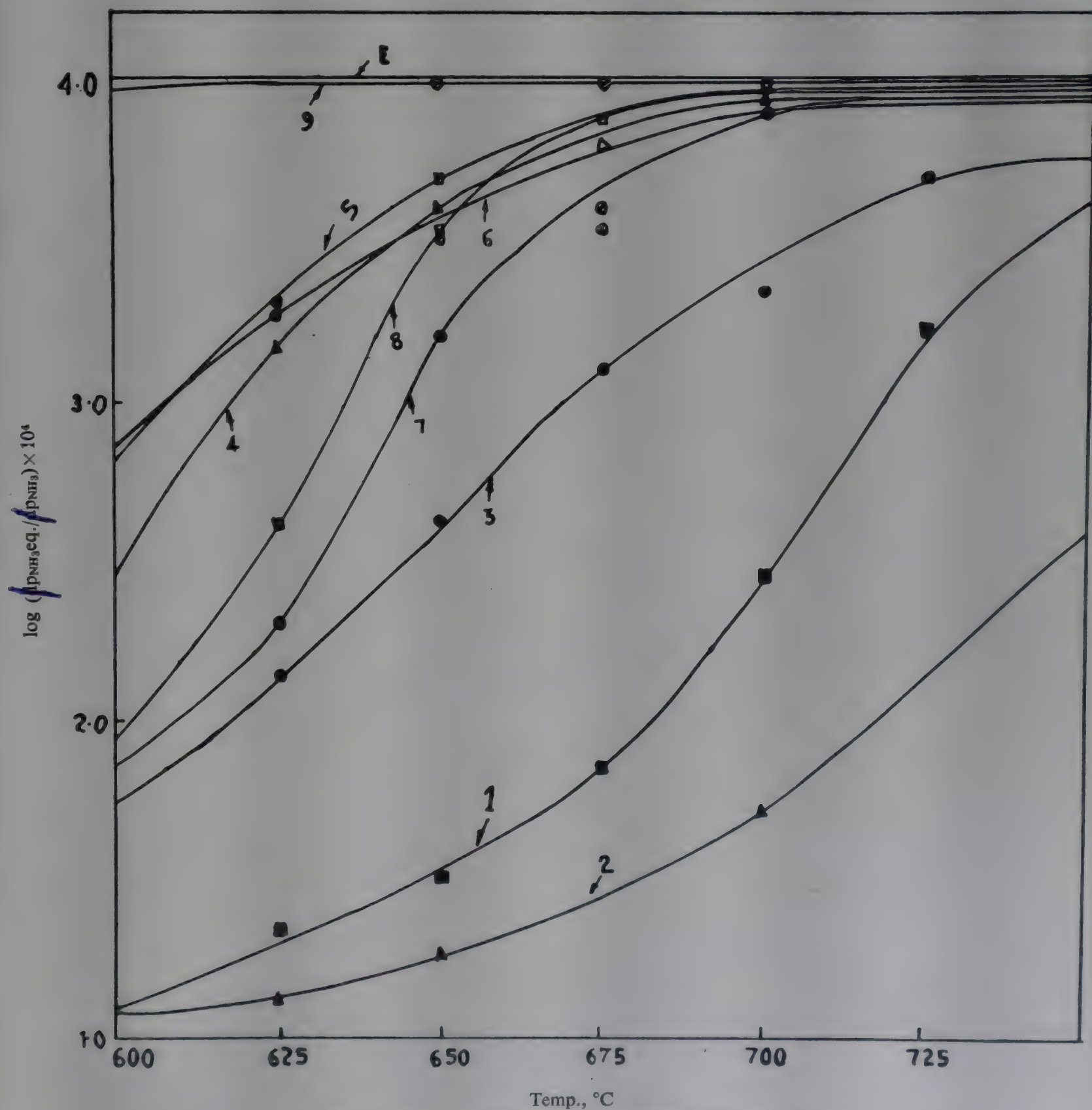


Fig. 2—Equilibrium Approaches at Different Temperatures

temperatures. In fact, this catalyst gives conversion very close to equilibrium even at the lowest temperature of the experiment, viz. 600°C. Further increase in temperature with this catalyst is of no advantage as the reaction is very close to equilibrium and the corresponding ammonia leakage is already very low at 600°C. The remaining eight samples of catalysts used in this experiment have shown very wide difference in activity at lower temperatures, the approach to equilibrium in all cases being much less compared to that of magnetic iron oxide.

However, these differences in activities decrease considerably with increase in temperature, and at temperatures above 700°C all the catalysts, except samples 1 and 2, give conversions near to equilibrium. From these observations, it is obvious that while the promoted magnetic oxide of iron can be efficiently used as a catalyst for ammonia decomposition at temperature as low as 600°C, the other catalyst samples, except 1 and 2, can be used with more or less equal efficiency only at temperatures above 700°C. Therefore, for industrial application, promoted magnetic oxide of iron is undoubtedly the most suitable catalyst of all the nine samples tested.

Activities of Catalysts at Different Temperatures: Let us now examine the variation in the activities of the different catalyst samples at different temperatures of experiment and the probable factors responsible for such variations. The samples of iron balls and calcined alumina rods (samples 1 and 2), which are not catalysts in the true sense, were chosen for the experiments to determine the effect of thermal conductivity of the contact material on an endothermic process like ammonia decomposition. Thermal conductivity of metallic iron balls is much higher than that of alumina rods. It can be seen from Table 1 that the specific surface area of iron balls is almost negligible whereas that of alumina rods is fairly high. From the activity results in terms of ammonia leakage as shown in Table 2, it is observed that both iron balls and alumina rods show equally poor activity at 600°C. But the increase in the rate of decomposition of ammonia with increase of temperature is much higher with iron balls than that with alumina rods. The low activity of alumina rods, in spite of high specific surface area, is probably due to lack of active components on the surface and poor thermal conductivity. With sample of iron balls, the poor activity at lower temperatures is apparently due to very low surface and rapid increase in rate of decomposition with temperature can be attributed only to its high thermal conductivity.

On comparing the activities of the four catalyst samples of nickel on alumina type (samples 3, 4, 5 and 6), it can be seen that the activity of such catalysts at any tempera-

ture within the range of experiment increases with increase in nickel content. Exceptions can be observed in the case of catalyst containing 20 per cent nickel (sample 6) with which the activity is found to be less compared to those with 5 and 10 per cent nickel at 650°C and above. Similarly, with the two iron on alumina type catalysts (samples 7 and 8), the activity increases with iron content.

With all the catalysts (except sample 9), considerable increase in the rate of decomposition with increase of temperature is observed. But the extent of increase is different with different catalysts. This is possibly due to two reasons. Firstly, from thermodynamic considerations, the effect of temperature on increase in rate of reaction will be more when the reaction is more away from the equilibrium. So, in the case of a catalyst with which the extent of decomposition is less at lower temperatures, the increase in the rate of reaction with temperature is more. Secondly, from thermal considerations, it is obvious that with a contact material having higher thermal conductivity, the increase in temperature causes comparatively higher rate of heat flow resulting in more increase in the rate of reaction. This explains the maximum increase in the rate of decomposition with temperature in the case of iron balls having the highest thermal conductivity of all the samples.

Thermal and Catalytic Factors: A possible explanation to the close efficiency of all the samples at higher temperatures in spite of wide difference at lower temperatures may be found in the following lines.

In the case of a catalytic process, two factors play part in determining the rate of reaction, viz. catalytic and thermal factors. While the former plays a vital role in all contact catalytic reactions, the thermal factor is important in the case of endothermic processes.

The influence of the thermal factor depends much on the heat flux to the reaction sites and increases with increase in temperature. But the catalytic factor depends much on surface activity of the contact material. Thus, at lower temperatures where influence of thermal factor is comparatively less, the rate of an endothermic reaction depends mostly on the catalytic factor of the contact material. The wide difference in ammonia leakage at lower temperatures of experiment with different contact materials, therefore, appears to be due to wide difference in their catalytic activity towards ammonia decomposition.

Again, the increase in the rate of reaction with temperature is mainly due to increased influence of thermal factor and a point may be reached when the catalytic

factor is relatively insignificant and the rate is controlled by the thermal factor. This was also suggested by Kazeev¹¹ in his studies on catalytic steam-methane reformation. So, for correct evaluation of the catalytic efficiency of the different contact materials in an endothermic process, it is essential to compare their activities at lower temperatures, where thermal factor is not predominant.

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Alkalized iron catalyst consisting of precipitated iron oxide and 15-20 per cent alkali as carbonate has been developed as a substitute of COMOX for hydrogenation of organic sulphur compounds in semi water gas. The influence of temperature and space velocity has been investigated to determine the optimum conditions for hydrogenation. In addition, a system comprising alkalized iron and zinc oxide has been studied for the removal of sulphur compounds from semi water gas.

Alkalized iron shows the maximum activity with respect to organic sulphur conversion at 400°C. Upto 10,000 space velocity activity is independent of time of contact. The combined system of alkalized iron and zinc oxide is effective for sulphur removal for a fairly long time and efficiency drops to 47 per cent after 4500 hours. The basic chemistry of hydrogenation and the process of activation of alkalized iron have been discussed briefly.

A Catalytic Process for the Removal of Organic Sulphur Compounds from Gas Stream

By N. C. MEHTA, T. S. R. PRASADA RAO, S. K. SINGH,
N. BHATTACHARYYA AND S. P. SEN,

*Planning & Development Division,
Fertilizer Corporation of India Ltd. Sindri, Bihar*

Introduction

Commercial gases like semi-water gas, coke oven gas, natural and refinery gases contain both inorganic and organic sulphur compounds, the concentration of which vary over a wide range depending upon the source of the raw material¹. The concentration of hydrogen sulphide, ranges between 400 and 1500 ppm and of

organic sulphur between 50 and 200 ppm. The principal organic sulphur compounds present are carbonyl sulphide, carbon disulphide, mercaptans and thiophene. The presence of sulphur compounds in industrial gases beyond certain limits is objectionable because in most of the chemical industries these gases undergo a catalytic operation and it is essential to render them free

from sulphur compounds which act as catalyst poison. Liquid-wash and dry-box purification processes² remove completely hydrogen sulphide but not organic sulphur compounds. In the production of synthesis gas by the traditional coal gasification process, where only high temperature CO-conversion catalyst followed by water-scrubbing and liquid-wash are used, any special treatment of the process gas for the removal of organic sulphur compounds is not necessary. With the introduction of low-temperature CO-conversion catalyst³ in the process for synthesis gas manufacture, the complete removal of sulphur compounds both inorganic and organic—down to the level of 0.1 ppm has become a basic need as this catalyst is highly sensitive to sulphur-poisoning.

Over the years, a wide variety of catalyst formulations have been suggested from time to time for the removal of organic sulphur compounds from gases⁴. The first catalytic process used commercially for the removal of such compounds was developed by Carpenter⁵ and Evans,⁶ using a nickel sulphide as the catalyst. Trutnuscici⁷ described the use of nickel turnings for the removal of small amounts of organic sulphur compounds from coal gases. Holmes-Maxted process⁸ employs a catalyst consisting of a metal thiomolybdate which converts organic sulphur compounds to hydrogen sulphide by hydrogenation. Key and Eastwood^{9,10} described two catalysts for organic sulphur removal from water and coal gases. Several other catalysts described in literature include chromia-alumina, copper-alumina and copper-chromium-vanadium¹¹ catalysts. Apart from these catalytic formulations, one of the most widely used process for the removal of organic sulphur compounds was the use of mixture of iron oxide and sodium carbonate. This process described by Sands *et al*¹² was first disclosed in Germany and was subsequently used in many commercial operations^{13,14}. But in the later years, a cobalt-molybdenum catalyst, known as COMOX, is most commonly used in commercial operations for the removal of organic sulphur compounds from hydrocarbon streams and also from gases².

The use of cobalt-molybdenum catalyst for the removal of organic sulphur compounds has been studied in this laboratory also, but its commercial production was not encouraged as the raw materials were not available in the country. Keeping in view the high costs of cobalt and molybdenum, a programme was taken in hand to develop a catalyst which is based on raw materials available indigenously.

In this paper the study of a catalytic process for the hydro-desulphurization of semi-water gas by two cata-

lysts prepared from indigenously available raw materials has been described. The semi-water gas has been chosen as the feed stream. The process is essentially a 2-stage one, the first stage involving hydrogenation of organic sulphur compounds over an alkalized iron catalyst and the second being absorption of hydrogen sulphide formed by zinc oxide. As feed gas itself contains a sufficient amount of hydrogen, the addition of hydrogen from external source is not necessary.

Experimental

(i) *Preparation of Alkalized Iron Catalyst*: Catalyst was prepared by precipitating iron carbonate from iron sulphate solution by alkali. The precipitated mass was washed till free from soluble impurities and heated to 120°C. Iron oxide so obtained was mixed with 15-20 per cent alkali in the form of carbonate. The resultant mixed mass was dried at 130-150°C, granulated and tabletted into 6×6 mm size of cylindrical shape, having bulk density 1.3-1.4 kg/l, surface area 40-50 m²/g and alkali content ranging between 15 and 20 per cent.

(ii) *Preparation of Zinc Oxide Catalyst*: This oxide was prepared from zinc nitrate by precipitation and subsequent heat treatment. The finished oxide has the bulk density of 1.2-1.3 kg/l and surface area 40-45m²/g. It contains 10 per cent ferric oxide.

(iii) *Feedstock*: The semi-water gas has the following composition (per cent): carbon monoxide 30-32, carbon dioxide 8-11, hydrogen 34-38, nitrogen 20-26, methane 0.8, oxygen 0.2 and hydrogen sulphide nil; organic sulphur 50-200 ppm.

(iv) *Procedure*: 50 c.c. of the alkalized iron and zinc oxide catalysts were charged in the reactors R1 and R2 respectively (Fig. 1). The catalyst beds in each reactor were supported on mullite packing at the desired heating zone of the furnace. The support also serves as a distributor avoiding channeling at the bottom layer of

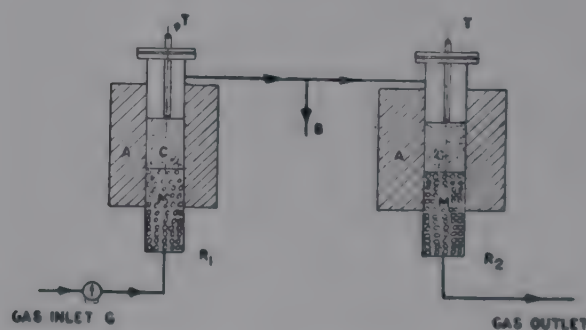


Fig. 1—Schematic Diagram of the Catalyst Testing Unit

A—Furnace	M—Mullite Packing
R ₁ —Reactor I	T—Thermo-couple
R ₂ —Reactor II	B—Bypass exit
C—Catalyst Bed	G—Gas meter

the catalyst. The upper end of the reactor was covered by a blank flange provided with a welded thermocouple sheath. Chromel-alumel thermocouple was used for measuring the temperature.

During the start-up of the experiment, the reactor was gradually heated in a nitrogen stream till it reached a working temperature of 400°C and the system got stabilized. Nitrogen supply was now turned off and the feed gas was introduced in the reactor at a fixed rate. At intervals, the concentrations of organic sulphur and hydrogen sulphide in the exit as well as feed gases were estimated.

(v) *Analysis*: Organic sulphur in the gas has been determined by a method described by Rogers and Baldaste.¹⁶ The amount of hydrogen sulphide was determined by its absorption in cadmium acetate and then titrating by an iodometric method.

Results and Discussion

In the present investigation, alkalized iron has been used as a primary catalyst in the first stage and zinc oxide absorbs hydrogen sulphide in the second. The influence of basic parameters, like temperature and space velocity, on conversion efficiency of the alkalized iron has been studied to evaluate the optimum conditions for hydrogenation. Efficiency of the combined system has been assessed separately.

Basic Chemistry in Hydrogenation: The process gas used comprises mainly carbon disulphide, mercaptan, carbonyl sulphide and thiophene while other substituted sulphur compounds were absent. The principal chemical reactions taking place in the hydrogenation may be expressed as

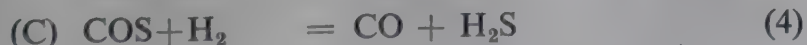
(A) Carbon disulphide



(B) Mercaptan



where R is an alkyl group, like CH₃, C₂H₅, etc.



In addition to the above, the following reactions may also take place which will deposit carbon on the catalyst surface.



The following hydrolysis reactions are also possible in the presence of moisture.



The process gas used in the present investigation was substantially free from moisture; therefore reactions 7 and 8 are of little significance here.

Hydrogenation of carbonyl sulphide is endothermic and that of carbon disulphide and mercaptan exothermic. Where all these compounds are present it is evident that the effect on final purity will depend on the relative concentrations of the compounds in the feed. The influence will be more pronounced at higher concentration of carbonyl sulphide. Actually very little work has been done so far to establish the relative rates of hydrogenation of sulphur compounds. Griffith *et al*¹⁷⁻¹⁹ have studied atmospheric pressure hydrogenation of carbonyl sulphide and carbon disulphide at a relatively low temperature. Hydrogenation of the former was found faster than that of the latter. The feed gas used here contains appreciable proportion of oxides of carbon, which affect the hydrolysis reaction and hydrogenation of carbonyl sulphide. As the gas is practically dry and contained only traces of carbonyl sulphide, oxides of carbon are not likely to have any significant influence on the final purity of the treated gas. This is confirmed by the results which show that almost complete conversion of sulphur compounds to hydrogen sulphide is possible when the catalyst is fresh. Slip of increasing organic sulphur compounds in the later stage is the result of fall in activity of the catalyst, which may either be due to fouling of the active sites by impurities or by reaction products (reactions 5 and 6). The deposition of elemental carbon on active sites will lead to a progressive deactivation of the catalyst activity with the proportional increase in unconverted sulphur in the treated gas.

Alkalized iron has been used for oxidation of organic sulphur compounds, where a small dose of oxygen is introduced with the feed. The conventional iron oxide catalyst with chromium oxide has been found to catalyse conversion of organic sulphur compounds simultaneously with shift reaction. Though there is considerable information on the mechanism of shift reaction, very little is available on the mechanism of hydrogenation of sulphur compounds by shift catalyst in presence of steam. The operating conditions of alkalized iron, however, are quite different than those of shift catalyst. Moisture is practically absent in the system. It is known that Fe₃O₄-phase is the active form of iron in shift

reaction, but when the steam concentration falls below a minimum limit in the system, oxide is further reduced to a lower state and finally to the metallic state. Alkalized iron contains 15-20 per cent alkali as sodium carbonate and does not contain any oxide of chromium. A highly reducing gas only saturated at the ambient temperature is likely to reduce the catalyst to the metallic stage. The presence of reduced iron in the system, if any, will catalyse the methanation reaction and methane content of the treated gas should increase. It has been seen, however, that the methane content of the gas stream remains practically unchanged. From this observation, it may be concluded that presence of reduced iron after activation, even if there is any, is not a major phase. Further study to elucidate the mechanism of hydrogenation is in progress.

Effect of Temperature on Activity: The results of experiments carried out at various temperatures in the range of 200-500°C are presented in Table 1. In all these experiments space velocity has been maintained constant at 500 (v/v hr¹). The effect of temperature has been

studied in three stages initially when the catalyst is fresh and after 200 and 500 hours of operation when the catalyst is partially deactivated. This was done on the assumption that with falling activity, after a period of run, increase of bed temperature might have a beneficial effect on the activity and may maintain the purity of the treated gas at the desired level. The activity of the catalyst has been expressed as percentage conversion of organic sulphur compounds in the feed.

It is observed that the activity of the catalyst increases with temperature, passes through a maximum and then drops. With a fresh catalyst, conversion is 81 per cent at 200°C bed temperature and it is virtually complete at 400°C; with further increase of temperature, it falls to 95 per cent at 500°C. The activity changes with aging of the catalyst in use but the trend with regard to influence of temperature on conversion efficiency remains identical in all stages of operation and the maximum conversion is always achieved at 400°C bed temperature. After a period of run even with increased bed temperature, complete conversion was not possible. After 200 and 500

TABLE 1—EFFECT OF TEMPERATURE ON ACTIVITY OF ALKALIZED IRON CATALYST

(Specific Velocity 500)

Number of Hours of Run	Temp., °C	Amount of Organic Sulphur in Feed Gas, ppm.	Amount of Organic Sulphur after Desulphurization, ppm	Organic Sulphur Conversion, %
Immediately after start-up	200	130	24	81
	250	130	20	84
	300	130	12	90
	350	130	Traces	Almost 100
	400	130	Traces	-do-
	450	130	3	98
	500	130	7	95
200	200	140	36	75
	250	148	31	79
	300	148	28	81
	350	148	14	89
	400	148	12	91
	450	148	18	88
	500	148	23	85
500	200	127	36	68
	350	127	34	72
	300	127	32	74
	350	127	21	83
	400	127	18	85
	450	127	22	82
	500	127	28	78

hours of run, maximum conversion was 91 and 85 per cent respectively.

Effect of Space Velocity: The effect of space velocity has been studied over a wide range starting from, 1000, to 15,000 vols. of gas/vol cat./hr. The results (Table 2) on fresh catalyst have been compared with the corresponding data after 200 and 500 hours of run.

It is observed that the conversion efficiency of the fresh catalyst remains unchanged over a wide range of space velocity and upto 10,000 s.v., treated gas was practically free of organic sulphur compounds. This shows that the conversion efficiency of the fresh catalyst is independent of the time of contact upto a limiting value corresponding to 10,000 s.v. The activity of the catalyst, however, changes with time in use, though with a fresh catalyst conversion of organic sulphur is almost complete at 10,000 space velocity and for the same space velocity the corresponding efficiency after 200 and 500 hr. is 84 and 73 per cent respectively. The deterioration of activity appears to be a function of degree of fouling of the active sites by reaction products.

It may be observed that the rate of hydro-desulphurization decreases with increasing space velocity, but the effect of changing space velocity is not uniform throughout the entire period of run. For a fresh catalyst the fall in activity is sharp above 10,000 s.v. but the effect is less pronounced in case of the old catalyst. As can be seen from Table 2, when the space velocity is changed from 10,000 to 15000, conversion of organic sulphur drops by nearly 20 per cent for a fresh catalyst, whereas for an identical change in space velocity corresponding drops are only 9 and 8 per cent respectively after 200 and 500 hours of run.

Results of a Two-Stage Process: In this process two catalysts were used, zinc oxide was placed next to alkalized iron in series. The purpose of placing zinc oxide is to remove the residual hydrogen sulphide present in the gas stream from the first bed. Semi water gas carrying organic sulphur compounds only was passed over the catalyst beds maintained at 400°C. To evaluate the comparative efficiency the process was studied at two space velocities, viz. 500 and 1000, and continued till the

TABLE 2—EFFECT OF VARIOUS SPACE VELOCITIES ON THE ACTIVITY OF ALKALIZED IRON CATALYST AT 400°C

Hours	Space Velocity	Organic Sulphur in Feed Gas, ppm	Organic Sulphur in Exit Gas, ppm v/v	Organic Sulphur Conversion
Immediately after startup	1000	200	Traces	About 100
	2000	200	-do-	-do-
	5000	200	-do-	-do-
	10,000	200	-do-	-do-
	15,000	200	5	80
200	1000	187	14	92
	2000	187	14	92
	5000	187	19	89
	10,000	187	29	84
	15,000	187	46	75
500	1000	172	31	82
	2000	172	31	82
	5000	172	36	79
	10,000	172	47	73
	15,000	172	60	65

conversion efficiency of the alkalized iron bed dropped to about 50 per cent of its initial value (Tables 3 & 4).

It was observed that almost complete desulphurization of the feed gas containing organic sulphur varying from 53 to 148 ppm is possible by the 2-stage process. At a space velocity of 500, the process is effective for 1500 hours for supplying a gas practically free of sulphur whereas at 1000 s.v. sulphur slip occurs after 1000 hours' run, and after this period sulphur starts appearing in the treated gas and increasing with the time of opera-

tion. When the space velocity of the system is 500, the purifying efficiency of the system drops to 47 per cent after 4500 hours (Table 3). At this stage, the treated gas contained 20 ppm unconverted organic sulphur and 16 ppm hydrogen sulphide with 68 ppm of organic sulphur in the feed stream. Therefore, though the overall efficiency of the system for removal of sulphur compounds dropped to 47 per cent, hydrogenation activity is still as high as 70 per cent.

Hydrogen sulphide is absorbed completely by alka-

TABLE 3—DESULFURISATION OF SEMI-WATER GAS BY ALKALIZED IRON AND ZINC OXIDE
(Temp., 400°C; Space Velocity 500)

Hours	Sulphur Content in Feed Gas, ppm v/v		Sulphur Content Exit Alk. Iron ppm v/v		Conversion of Org-Sulphur After Ist Stage, %	Sulphur Content in Exit, ZnO, ppm v/v		%Conversion of Organic Sulphur After Ist Stage, %
	Org.S	H ₂ S	Org.S	H ₂ S		Org.S	H ₂ S	
Nil	130	Nil	Traces	Nil	Almost 100	Not Traceable	Nil	Almost 100
100	145	-do-	5	Nil	96	-do-	-do-	-do-
500	148	-do-	15	-do-	89	-do-	-do-	-do-
1000	100	-do-	20	-do-	80	-do-	-do-	-do-
1500	125	-do-	28	10	77	-do-	-do-	-do-
2000	53	-do-	15	17	71	3	-do-	94
2500	64	-do-	19	23	69	5	-do-	92
3000	75	-do-	26	30	65	8	5	89
3500	60	-do-	23	40	61	10	8	83
4000	66	-do-	31	45	53	15	12	77
4500	68	-do-	34	48	50	20	16	70

TABLE 4—DESULFURISATION OF SEMI-WATER GAS BY ALKALIZED IRON AND ZINC OXIDE
(Temp., 400°C; Space Velocity 1000)

Hours	Sulphur Content in Feed Gas, ppm v/v		Sulphur Content Exit Alk. Iron, ppm v/v		Conversion of Org-Sulphur After Ist Stage, %	Sulphur Content in Exit, ZnO, ppm v/v		%Conversion of Organic Sulphur IInd Stage, %
	Org.S	H ₂ S	Org.S	H ₂ S		Org.S	H ₂ S	
Nil	126	Not Traceable	Traces	Nil	Almost 100%	Not Traceable	Nil	Almost 100%
100	130	-do-	5	-do-	95%	-do-	-do-	-do-
500	100	-do-	9	Traces	81	-do-	-do-	-do-
1000	125	-do-	20	9	71	-do-	-do-	-do-
1500	117	-do-	40	19	65	3	-do-	97
2000	110	-do-	45	28	59	10	5	90
2500	130	-do-	58	56	55	18	16	86

lized iron bed in the initial stage, but its capacity for hydrogen sulphide retention dropped progressively with the passage of gas. It appears that there is a qualitative relation between hydrogen sulphide-retention capacity of the alkalized iron and its hydrogenation activity. With a decrease of conversion efficiency of organic sulphur, hydrogen sulphide slip from the bed increases. At a later stage of operation, alkalized iron bed not only ceases to absorb hydrogen sulphide but it also starts releasing hydrogen sulphide which is already absorbed in the bed (Table 3).

With the fall in activity of alkalized iron, load on zinc oxide bed increased progressively. But the second bed maintained a steady level of activity for a fairly long period and absorbed both organic sulphur and hydrogen sulphide. With the two-bed system, purity of the treated gas falls with the aging of the catalyst but about 90 per cent removal of sulphur compounds is possible for more than 2500 hours.

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Samples of zinc oxide containing varying amounts of iron oxide were prepared under identical conditions by thermal decomposition of carbonates and their surface areas were determined both before and after curing. It was found that the surface area increases with increasing iron content and attains a maximum at about 7 per cent ferric oxide (Fe_2O_3) content. A possible explanation seems to be the coverage of zinc carbonate particles during precipitation thus inhibiting their crystal growth.

Study of the System $\text{ZnO-Fe}_2\text{O}_3$

Part I—Dependence of Surface Area On Fe_2O_3 Content

By R. M. MOORJANI, P. K. SENGUPTA, G. SENGUPTA
AND S. P. SEN,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Use of zinc oxide for removal of hydrogen sulphide is a common practice in chemical industry. The removal takes place through sorption followed by chemical reaction between the adsorbate and adsorbent. Apparently it seems that the whole quantity of zinc oxide should react to give zinc sulphide. But in actual industrial operation this is not the case. In fact, zinc oxide of different make vary widely in rate of hydrogen sulphide pick up. This is because in a flow system the time of contact is an important factor in determining the rate of reaction. This again is associated with the surface area of the adsorbent. The method of preparation of zinc oxide for commercial use should be such that a large surface area is obtained. Several authors have suggested different methods for preparing high surface area zinc oxide. Krause and Plura¹ have treated zinc carbonate with liquid air and then thermally decomposed it to zinc oxide. Takahashi and Tsutsumi² have shown that the surface area of zinc oxide can be increased by grinding. Shekhter and Zhabrova³ prepared zinc oxide by decomposition of zinc carbonate at 350°C in vacuum.

In preparing active catalysts with high and stable surface area promoters are usually added to get the desired result. In case of zinc oxide desulphurizing agents we find that quite a good number of commercial variety contain an appreciable amount of ferric oxide. The present investigation was started with a view to find out the effect of adding ferric oxide upon the texture and other properties of zinc oxide.

Experimental Procedure

Preparation of Samples: Zinc carbonate containing 0 to 10 per cent w/w ferric oxide was precipitated (sample Nos. 1 to 5) from a solution containing zinc nitrate and ferric nitrate. The precipitate was filtered, washed and dried in air at 120°C for 12 hours. The dried samples were cured at 300°C for 4 hours. A sample of ferric oxide was prepared under identical conditions for use as reference. The sample was marked 'R'.

Thermogravimetric Analysis: The rate of decomposition of sample Nos. 1 and 5 (uncured) at 200°C was studied with the help of a Stanton Mass Flow Thermobalance with a sensitivity of 0.2 mg. The weight-loss measurements were carried out with 100 mg. of the sample heated in a stream of dry nitrogen. The temperature was slowly raised to 150°C and held steady till all the moisture had been driven out and no further loss occurred. The temperature was then raised to 200°C and rate of weight loss was recorded automatically. The results are represented graphically as the variation of fraction decomposed (α) with time (t) (Fig. 1) and the variation of rate of decomposition ($d\alpha/dt$) with time (t) (Fig. 2).

Differential Thermal Analysis: DTA measurements of uncured samples were carried out with the help of a Linseis Differential Thermal Analyser. The samples were taken in Pt crucibles provided with Pt/Pt-Rh (13 per cent) thermocouples. Ignited alumina was used as reference. The thermograms of all the samples from 1 to 5 were found to be similar in nature (Fig. 3 A). Thermogram of

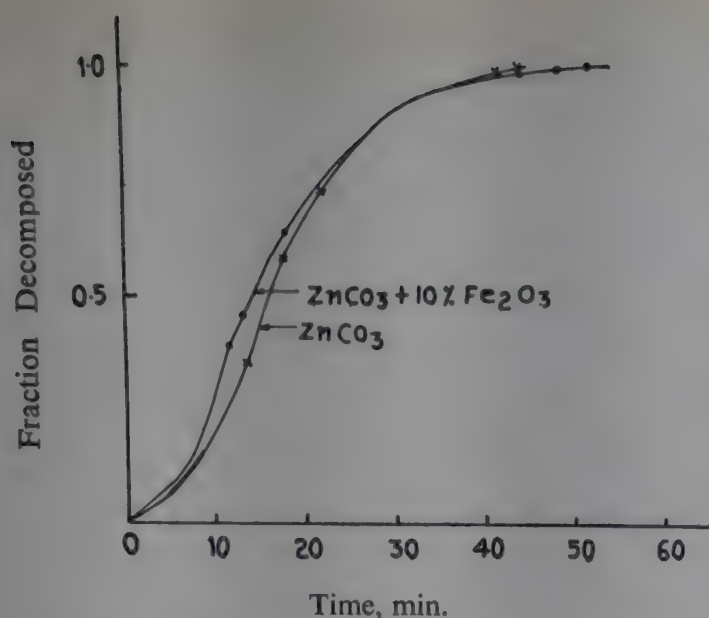


Fig. 1—Variation of Fraction Decomposed with Time

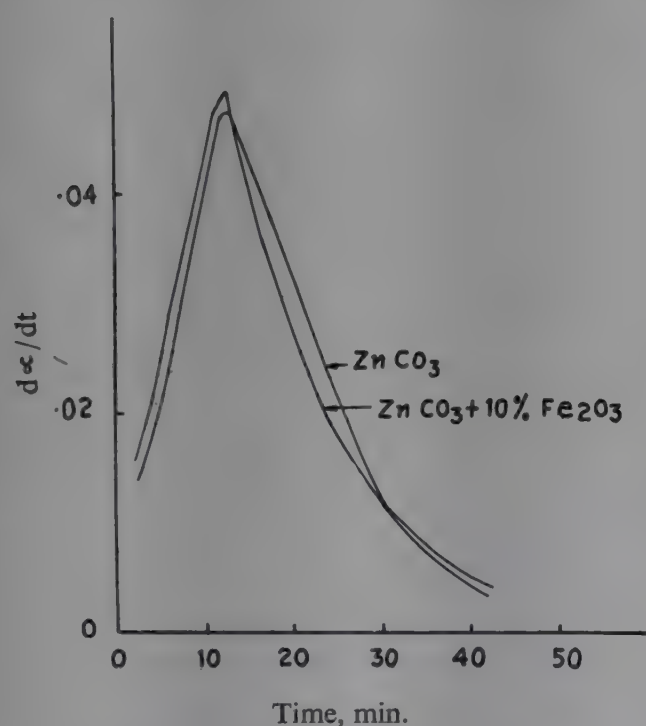


Fig. 2—Variation of Rate of Reaction with Time

sample (R) was also recorded for reference (Fig. 3B).

X-Ray Measurements: X-ray photographs of both cured and uncured samples were taken with the help of a Russian x-ray unit using Fe K α radiation.

Surface Area and Particle Size Measurements: Surface areas of the samples were determined by BET method using nitrogen as adsorbate. The area of cross section of nitrogen molecule was taken to be 16.2Å². An apparatus similar to that described by Kokes⁴ was used for helium density measurements. Average grain size was calculated from helium density and surface area data⁵.

The results for both cured and uncured samples are presented in Table 1. The variation of surface area with increasing ferric oxide content is presented graphically in Fig. 4.

Results and Discussion

From the plot of α vs t and $\frac{d\alpha}{dt}$ vs. t (Figs. 1 and 2 respectively) it can be seen that the rate of decomposition of zinc carbonate is increased in presence of ferric oxide. The nature of the graphs clearly shows that the reaction

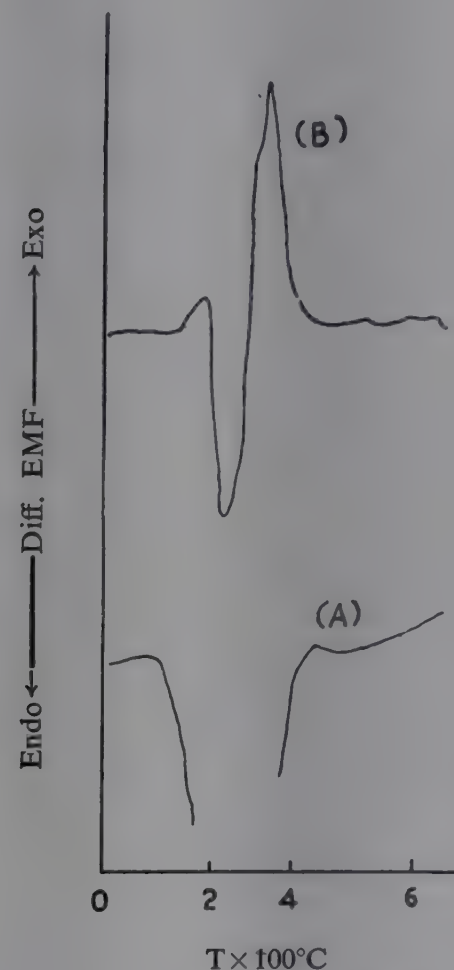


Fig. 3—DTA Thermogram

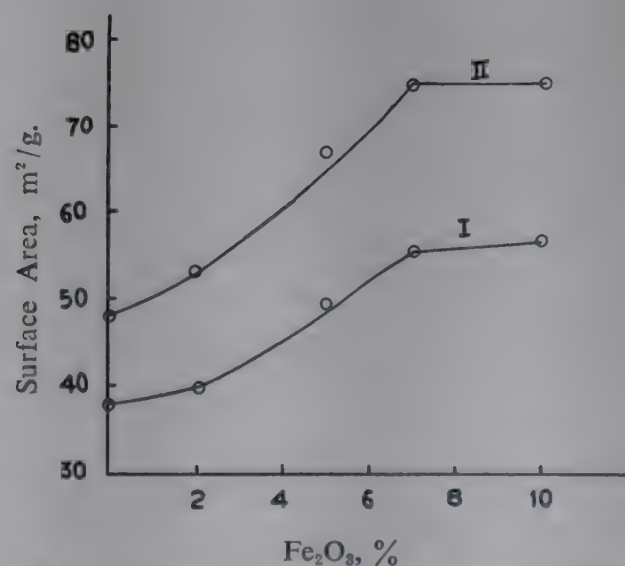


Fig. 4—Variation of Surface Area with Fe₂O₃ Content
I—Uncured Samples II—Cured Sample

TABLE 1

% Fe ₂ O ₃	Surface Area, m ² /g.		He displacement, cc./g.		Particle Size, Å(r)		Decrease in Particle Size, %
	Uncured	Cured	Uncured	Cured	Uncured	Cured	
0	37.8	48.2	—	—	198.4	118.2	40
2	39.4	53.0	—	—	190.5	107.5	43
5	48.9	66.9	0.25	0.19	153.4	85.4	44
7	55.2	74.7	—	—	135.8	76.3	43
10	56.6	74.8	—	—	132.5	76.2	42

$$\% \text{ decrease in particle size} = \frac{r_{\text{uncured}} - r_{\text{cured}}}{r_{\text{uncured}}} \times 100$$

is autocatalytic in nature. The initial rate is slow but then increases as more and more product is formed. Following Langmuir⁵ the behaviour can be readily explained if it is assumed that the reaction takes place at the linear interface between the two solid phases. The reaction rate will be small at the beginning due to the absence of the necessary interface but increases rapidly as the reaction progresses. A similar mechanism has been proposed by Betsznaajders and Cibor⁷ in deriving the kinetic expression for the thermal decomposition of ZnCO₃ at 1 atm pressure. Addition of ferric oxide increases the number of suitable interfaces, thereby increasing the rate of reaction. The fact that the nature of α vs. t curve is not altered by the presence of ferric oxide indicates that addition of ferric oxide only accelerates the decomposition process and does not affect the mechanism of the process.

From Fig. 4 it can be seen that the surface areas of uncured samples 1 to 5 increase with increasing ferric oxide content upto a concentration of 7 per cent. Further increase of ferric oxide content to 10 per cent has little effect upon surface area. A probable explanation for the phenomenon is that during coprecipitation the particles of zinc carbonate get covered with a protective layer of ferric oxide which retards (1) the rate of nucleation, (2) rate of crystal growth and (3) the aggregation of primary particles. All these factors will obviously decrease the grain size of zinc carbonate particles. Once all the zinc carbonate particles are completely covered with a layer of ferric oxide, further addition of ferric oxide has no effect. The protective action of ferric oxide in this case can be compared with the stabilization of lyophobic colloids by lyophilic colloid.

From Table 1 and Fig. 4 it can also be seen that upon curing the surface area of samples 1 to 5 increases continuously upto a ferric oxide concentration of 7 per cent. Moreover the percentage decrease in particle size upon

curing (column 8, Table 1) are of the same order of magnitude for all the samples which indicates that the presence of ferric oxide does not affect the crystal growth of zinc oxide.

The DTA diagram (Fig. 3B) of uncured ferric oxide (sample R) shows that of the two peaks one is endothermic at 210°C and the other exothermic at 310°C a behaviour typical of hydrated α -Fe₂O₃.^{8,9} The endothermic peak corresponds to that of dehydration and the exothermic peak corresponds to the transformation of dehydrated microcrystals of α -Fe₂O₃ to large crystals. X-ray data also indicate that iron oxide is present as α -Fe₂O₃.

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Influence of free space or 'ullage' on the drop test performance of polyethylene-lined jute bags filled with 50 kg of fertilizer have been investigated. The results indicate that the bags are more susceptible to damage with insufficient 'ullage'. The effect is marked in the case of 'Face drop'. The extent of free space desirable is given and the results discussed. Furthermore the damage is found to be chiefly on account of seam failure.

Influence of 'Ullage' on the Strength of Polyethylene-Lined Jute Bags

By D. K. SEN, SURENDRA MOHAN AND S. VARMA,

*Planning & Development Division,
Fertilizer Corporation of India Ltd. Sindri, Bihar*

Ever since polyethylene-lined jute bags were first introduced¹ in this country for packing ammonium sulphate-nitrate and urea, it has found general acceptance by the fertilizer manufacturers both of public and private sectors for packing purposes. The moisture impermeability of such a bag is imparted by a thin film of polyethylene and the strength is due to the jute part of the bag. Inherent advantages of such bags, over 'all plastic' or multiwall paper bags, under the present conditions of handling, storage and transportation, are listed elsewhere.² For a low cost product, such as fertilizer, it is necessary that the packaging cost is minimum. In an earlier communication³, it was pointed out that it is economical to design a bag for an optimum protection for a given fertilizer from the humid atmosphere prevalent in the region where the fertilizer is produced and marketed rather than fortifying the bag for the worst climatic condition and for the most hygroscopic product. Similarly, for economy the strength of the bag should just be adequate to withstand the rigours of handling without giving any 'over protection'.

Bag failures occur mainly on account of accidental or intended drops from varying heights on the varying nature of impact surfaces. This occurs while loading, unloading from various means of conveyance and during stacking, unstacking and additional handlings involved during transshipment of the fertilizer filled bags from one railway gauge to the other. Damage is also sometimes caused by the use of hooks which are forbidden, or as a result of a drop while loading on sharp edges or bolts of wagon or truck. The force of impact is clearly a function

of the total weight of the fertilizer-filled bag and the drop height. The bag dropped horizontally on one of its faces is termed 'face drop'. The bag dropped vertically on the bottom or top seam is known as 'butt end drop'. Sometimes a bag is dropped at an angle from shoulder height in a way which constitutes a throw rather than a drop and the filled bag lands itself on the bottom corner of one of its faces and constitutes 'lower end drop'.

The desirability of leaving optimum free space in the bag is often ignored though its effect on the strength of the bag is vaguely recognised. Moreover, less free space in the filled bag effects its stacking and handling characteristics. In the present series of experiments drop tests have been performed on the fertilizer filled bags with varying 'ullage' and an optimum free space needed is indicated which minimize the stresses undergone by the bags during these tests. As it is difficult to measure the free space in a stitched fertilizer filled bag, the following procedure was adopted: The bag was filled with 50 kg. of the fertilizer and the surface of the fertilizer was made plane. The height between the level of the fertilizer and the top end of the bag was measured vertically. After deducting 6 cms. as the top edges left out after stitching, the remainder was taken as a free space. The free space was decreased by increasing the length of mouth edge to the desired extent, keeping the weight of the fertilizer constant i.e. 50 kg.

Results

The drop test results show that a fertilizer filled bag survives a single drop from a specified height but fails

when dropped repeatedly from the same height. This is understandable as the jute is a fibrous material and each drop is liable to damage the fibres and thus weaken the threads constituting the jute cloth which ultimately snaps as a result of repeated stress. Thus the concept of drop number is applicable in the case of polyethylene-lined jute bags. The 'Drop number' is defined as the number of drops from a specified height which a bag withstands before its failure.

Table 1 gives the results of drop tests performed on polyethylene lined jute bags specification of which is given separately. The bags were dropped from a height of six feet by a gallows type of manually operated drop tester fabricated in our workshop on a concrete surface. The bags were dropped flat on their faces (face drop). It is evident that as the free space is progressively reduced there is a corresponding decrease in the 'Drop number'. The damage was mainly confined to the side seam. In Tables 2 and 3 the results are recorded when the fertilizer-filled bags were subjected to the 'butt-end' drops. A single drop from the height of six feet caused failure of the bag. When the drop height was gradually reduced to

TABLE 1

Free-space* length cm. (inch)	Number of drops from a height of 6.0 ft. (1.83 M)	Observation
20.00 (8.0)	16	No visible rupture or damage
16.50 (6.5)	6	Damaged along the side seam.
16.50 (6.5)	6	Damaged on the opposite face.
16.50 (6.5)	4	Damaged along the side seam.
14.07 (5.5)	2	Damaged on the opposite face.
11.41 (4.5)	1	Damaged along the side seam.
11.41 (4.5)	1	Damaged along the side seam.

*Length from the level of fertilizer along the side of the bag upto the line of stitching.

Specification of the bags used in the present series of experiments:

1. Type of Jute	D. W. tarpaulin; 10 × 10 shots and Porters; weight of the cloth 436 g/m ² (15 ozs/45")
2. Dimension	35" × 26" (89 cm × 66 cm)
3. Liner and Bounding	Polyethylene film of 25 μ laminated to jute with bitumin.
4. Stitches	Double lock stitch at the side and on the bottom. Ends externally folded and stitched. Minimum of three stitches per 2.5 cm.
5. Stitching yarn	Two-ply twist tyre cord.
6. Mouth	Selvadged.

TABLE 2—EFFECT OF FREE-SPACE ON BUTT-END DROP

Free-space length cm. (inch)	Dropped from a height of 3.0 ft. (0.915 M) Drop No.	Observation
22.86 (9.0)	4	
21.59 (8.5)	4	
20.32 (8.0)	3	
19.05 (7.5)	3	
17.78 (7.0)	4	
16.51 (6.5)	2	
15.22 (6.0)	2	
13.97 (5.5)	2	
12.70 (5.0)	3	
11.43 (4.5)	3	

Damaged along the side seam.

TABLE 3—EFFECT OF HEIGHT ON THE BUTT-END DROP

Dropping height feet (Metre)	Drop Number	Observation
6.0 (1.83)	1	
5.0 (1.52)	1	
4.5 (1.37)	2	
4.0 (1.22)	3	
4.0 (1.22)	5	
3.5 (1.07)	3	
3.0 (0.914)	4	
2.5 (0.762)	6	
2.0 (0.610)	12	

Damaged along the side seam.

No visible damage.

4 ft., the bag failure occurred after two consecutive drops; a height of 3 feet required four consecutive drops to cause the failure of the bag; consecutive 12 drops from a height of 2 feet did not visibly affect the bag. The damage was found in each case due to the failure of side seam. It is important to note that in no case the failure occurred due to the breakage of sewing thread or twine and the damage was confined to the failure of the threads constituting the jute cloth. The influence of free space or ullage was not found to be so marked in the case of butt end drop as with the face drop. Results further indicate that the stresses to which the bags are involved when subjected to the lower end drop are more akin to the face drop as shown in Table 4. In case of lower end drop damages are found to occur generally at the bottom seam. It is to be noted, however, that the impact during lower end drop seldom occurred at the same spot and thus there is liable to be a slight variation, even during drop tests, in the location of maximum stress and this fact may affect the drop number. The results indicate

TABLE 4—EFFECT OF FREE-SPACE ON ANGULAR FACE DROP

Free Space Length, cm. (in.)	Number of Drops from a Height of 6.0 ft. (1.83 M)	Observation
21.59 (8.5)	10	No rupture or damage was apparently visible.
21.59 (8.5)	10	
18.29 (7.2)	10	
18.29 (7.2)	10	
16.51 (6.5)	9	Damaged in the middle along the bottom seam.
16.51 (6.5)	8	
12.7 (5.0)	1	Damaged on the middle along the bottom seam.
12.7 (5.0)	1	

that (1) The influence of free space is marked in the case of face drop. Less free space causes side seam failure; (2) butt end drop is more damaging than face or side face drop and invariably leads to side seam failure; and (3) the cracks on the bag always occurred in the longitudinal direction along the length of the bag (side seam). Excepting in the case of lower end drop when the bottom seam gave way.

When a fertilizer-filled bag is dropped from a specified height on a concrete floor the impact energy is the kinetic energy generated due to its fall and the stress to which the bag is subjected to depend on the weight of the fertilizer, drop height and the area of contact between the bag and the impact surface. Part of the impact energy is dissipated on account of friction losses between the particles and a smaller part may even be absorbed by the impact surface and the rest is transmitted to the bag as the strain energy which causes the bag failure. The rheological behaviour of solids are not yet completely understood and the extent of dissipation of energy and the self-cushioning effect of particles is far from clear. Nevertheless, if the bag is loosely packed or sufficient free space is provided then the dissipation of impact energy would be more on account of the available space for the particles to rebound and readjust themselves and thereby dissipate a part of the impact energy. If, on the other hand, the bag is tightly packed and there is very little free space, the 'rebound dissipation' of energy is not possible and side bottom or top seam failure resulted as the strain energy caused stress concentration near the seams due to the curvature and/or due to the weakness of the seam itself. Seam failures in the present series of experiments normally occurred longitudinally, i.e. along the length of the bag. Bottom

and top seams failed when the drop at the instant of impact was not exactly flat but occurred slightly away from the centre on the bottom or top side. Another vulnerable spot is the mouth seam which may give way if the stitching is not properly done or the stitching thread is weak. In the case of butt end drop the column of particles above the impact layer is too high and the weight of the fertilizer prevents the "rebound dissipation" and therefore the bag failure is not so much dependent on the extent of ullage provided and the stress is concentrated on the side seam which fails longitudinally. Moreover, area of contact between the bag and the impact surface is minimum and thus the stress produced is more with the result that butt end drop proves more damaging.

An optimum 'ullage' of 18-20 cm. measured vertically along the side of packaging material from the level of the fertilizer to the position where stitching is to be done should be provided. This corresponds 10-12 cm when measured vertically (Fig. 1). This has been found to be adequate from strength as well as from handling and stacking considerations and takes into account any fluctuation in the bulk density arising out of a change in the process conditions or any possible variation in the particle size distribution between the product directly bagged and the material received from the silo. In this context, it is to be noted that the stresses developed in a filled bag during its handling are also dependent on the product characteristics. A bag containing hard lump or caked fertilizer is liable to get damaged under less severe

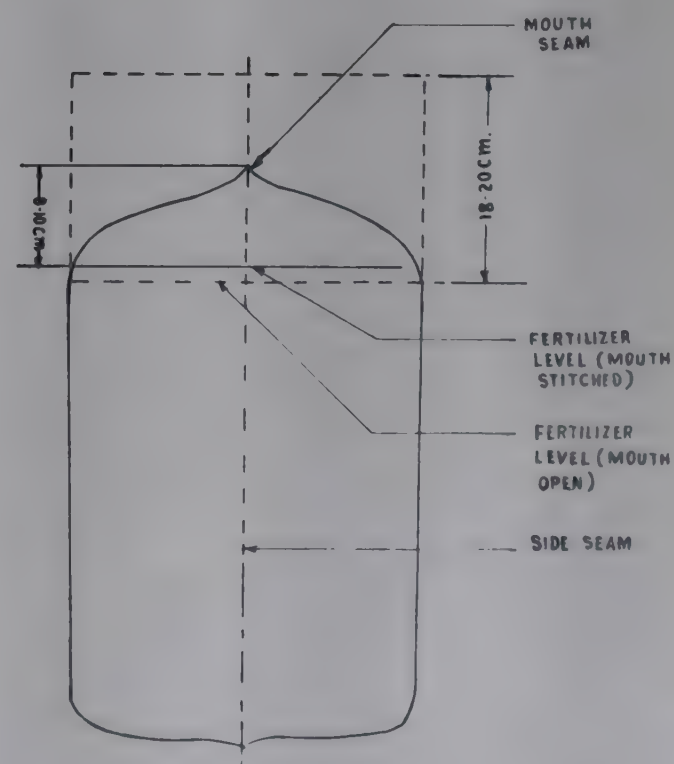


Fig. 1—Optimum Free Space in a Fertilizer-filled Bag

conditions of handling as there is hardly any dissipation of energy on account of friction between particles or the rebound of particles and the impact energy almost completely manifests itself as strain energy. On the other hand, if the lumps are soft part of the impact energy is spent in disintegrating the lumps and the stresses to which the bags are involved is not so severe. Free-flowing prills or granules lose considerable proportion of impact energy on account of friction losses and rebound dissipation.

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The carbon dioxide producing capacity of some soils, maintained under different treatments, has been studied. With all soils, the highest rate was noted during the first 24 hours after moistening air-dry soils, but this went on decreasing quite rapidly at first and later on slowly until after about 24 days, more or less a steady rate of carbon dioxide evolution of much lower value was obtained. Though the application of NPK fertilizers had improved the rate for a few days, this was not maintained for more than a week. The incorporation of chicken dropping into the soils, however, had increased the evolution rate markedly. Even after 31 days of incubation of soils with this treatment, the rate maintained was more than double of either the control or NPK-treated soils. It was concluded that the carbon dioxide-producing capacity of this soil with 0.34 per cent organic matter can be increased only through the input of organic matters.

Carbon Dioxide Evolution from Soils

Part I—A Preliminary Study

By A. C. DAS,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Though theoretical considerations may indicate an enormous reserve of carbon dioxide on the surface of earth, it has often been noted that the air layers surrounding field crops may frequently contain lesser concentration of this gas^{1,3-6} than the optimum amount necessary. It is quite probable that concentration of carbon dioxide under the field conditions may diminish at times and this short supply may be more pronounced during day-time, particularly when intensive photosynthesis takes place. The problems of uninterrupted supply of carbon dioxide to the growing crops, therefore, should not be overlooked. The loss of carbon dioxide from air through

photosynthetic utilization can be made up by wind movement, diffusion or evolution of the gas from soils. As carbon dioxide is a heavy gas and does not diffuse rapidly, soil has an important part⁸ to play as this is the nearest source to the growing crops. According to Lündegardth,² a good portion of carbon dioxide utilized by plants is obtained locally as a result of 'soil respiration'. This represents mainly the microbial activities leading to the decomposition of soil humus. In fertile soils, the rate of this decomposition is fairly high, resulting in the liberation of greater amount of carbon dioxide⁷. Thus, the question of soil fertility is closely linked up

with its ability to evolve carbon dioxide at a suitable rate.

In India, soil has been cultivated for centuries and its organic matter has been depleted to a great extent. Under the circumstances, the intensive use of artificial fertilizer for increased food production can only deteriorate the situation as this practice is likely to make a heavy demand on the meagre source of organic matter in soil and cause its further depletion. Apart from the harmful effects², this practice is likely to bring about on physical and physico-chemical properties, loss of soil structure, decrease in exchange and water-holding capacity of soils, the carbon dioxide-evolving capacity of soils is also likely to decrease. This is probably going to create a serious obstacle in all attempts for boosting up food production in Indian soils as the carbon necessary for high production may not be available.

A study was, therefore, undertaken in order to throw some light on the nature of carbon dioxide evolution from some soils low in organic matter and maintained under different treatments. Some observations so far made are discussed in the present communication.

Method and Materials

Soils had been collected from the recently developed farm plots, air-dried for about a month in the laboratory and the following treatments were then applied: (A) Soil + NPK, (B) Soil + Chicken droppings (C) Soil + NPK + Chicken droppings and (D) Control.

The following rates of fertilizer grade chemicals were used.

N (as Ammonium sulphate) at	50	mg./kg soil.
P (as Single Superphosphate) at	20	-do- -do-
K (as Muriate of Potash) at	20	-do- -do-
Chicken dropping (2.23 per cent N) at	2	g./kg soil.

50 g. of the treated soils were then moistened to about 40% per cent saturation and transferred to glass columns of about 600 ml capacity. This was then further moistened by adding calculated amount of water to bring moisture level to its 60 per cent saturation. The glass columns were then closed by rubber corks at the top and rubber tubing at the bottom and incubated at room temperature (28-32°C) for 24 hours. At the end of this incubation period, 5 l. carbon dioxide-free air (rendered carbon dioxide-free by passing air in series through Nesbitt tubes containing soda asbestos, 2N solution of caustic soda and water) was drawn through the column by applying suction and the outgoing air was then bubbled through a solution of barium hydroxide of known strength in the carbon dioxide estimating

glass apparatus. The amount of carbon dioxide so trapped was then estimated by back-titration of the barium hydroxide with a standard hydrochloric acid. The process was repeated after every 24 hours. Blank was maintained side by side and has been deducted from the results. Two experiments with two replications each were conducted and the mean results are given.

Results and Discussion

The rate of carbon dioxide evolution from soils maintained under different treatments are estimated and the data recorded in Table 1. It is quite evident that the carbon dioxide evolution rate is highest during the first 24 hours immediately after moistening the air dry soil but this enhanced rate goes on decreasing quickly at first but later on slowly till after about 24 days, more or less a steady rate is attained.

The application of only inorganic fertilizer, i.e. NPK, has increased the rate of carbon dioxide evolution for a few days as compared with the control but this higher rate has not been maintained for long and after about 7 days the amount of carbon dioxide evolved was more or less the same as that of the control soil. The application of chicken droppings, however, has increased this rate markedly. Though in this case as well the rate has declined in course of time but its superiority has been maintained throughout. Even after 31 days, the rate of carbon dioxide evolution (i.e. 1.91 mg. CO₂/24 hr.) from chicken droppings-treated soils is more than double than that of either control or NPK treated soils (i.e. 0.87-0.88 mg. CO₂/24 hr.). When chicken droppings were applied along with NPK, the rate of carbon dioxide evolution remained the same as with chicken droppings alone.

The amount of organic matter content of the present soil estimated by Walkley & Black's method was noted to be about 0.34 per cent. As this is a very low content, it is likely that the application of fertilizers alone was unable to maintain enhanced rate of carbon dioxide evolution for more than a few days due to the non-availability of organic carbon in soil for microbial decomposition. The application of chicken droppings has greatly increased the rate of carbon dioxide as this has supplied necessary organic matter for microbial activities and hence even after stabilisation reached in 24 days the rate of carbon dioxide evolution from chicken droppings treated soils is almost double than that of either control or NPK-treated soils.

Conclusion

The results so far discussed have shown that though a high rate of carbon dioxide evolution, i.e. 4.98 mg. CO₂/

TABLE 1—EVOLUTION OF CARBON DIOXIDE DURING 24 HOURS FROM 50 g. AIR-DRY SOILS
MOISTENED TO 60 PER CENT SATURATION, mg.

1	Soil Treatments			
	2	3	4	5
Incubation in days after moistening	Control	NPK	Chicken Dropping	NPK + Chicken Dropping
1	4.98	4.91	11.90	12.01
2	3.01	5.32	10.75	11.32
3	2.85	5.69	8.44	8.15
4	2.28	5.83	5.87	6.21
5	2.46	3.21	5.45	5.89
6	2.16	3.01	5.15	5.21
7	2.04	2.39	4.34	5.10
8	2.61	2.51	4.12	4.00
9	1.56	1.61	3.35	3.89
10	1.42	1.39	3.24	3.38
14	1.06	1.11	2.50	2.64
16	0.90	0.98	1.98	2.12
24	0.87	0.88	1.92	1.89
31	0.88	0.87	1.91	1.93

day/50g. soils, is noted immediately after moistening air-dry soils, this falls off quickly and in course of about 24 days stabilizes to a much lower value of 0.87-0.88 mg CO₂/day/50g. soils. Some improvements were recorded for the first few days by the application of NPK to the soils but this was not maintained after 7 days. Experiments were also conducted by using 2-4 ppm of some trace elements, like zinc, copper, boron, manganese, molybdenum and iron, along with NPK both individually and in combination but none of these combinations were noted to differ from the control so far as the rate of carbon dioxide evolution is concerned. Waksman,⁷ however, recorded a much higher rate by applying lime to some acid soils having pH of 4.9. As the present soil is already alkaline having pH 8.0-8.2, liming is likely not to produce any such effect. The process of alternate drying and wetting may increase the rate of carbon dioxide evolution from soils but under the field conditions with growing crops, this practice may interfere with the metabolic processes of crop plants due to shortage of water supply during drying. Thus, it seems quite certain that the use of organic manures only can improve the carbon dioxide-supplying capacity of the present soils having low content of organic carbon.

Under the circumstances, it seems imperative that along with the use of inorganic fertilizers a programme for supplying organic manures in moderate quantity or some suitable methods for building up soil organic matters should be adopted. As this will increase the carbon dioxide evolution rate, the yield potential of the

soil is also likely to improve. Studies however, are necessary in order to determine the optimum rate of carbon dioxide evolution attainable under the field conditions and the corresponding yield potential obtained. Further investigations on the above lines are in progress.

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Based upon high frequency titrimetry, a quick and accurate method has been developed for the estimation of nitric, phosphoric and hydrofluosilicic acids in solutions containing one, two or all of them together. The method consists in titrating very dilute solutions of these acids against a standard caustic soda solution with an oscillotitrator at 140 Mc/s. The method has been utilized in the quick estimation at any stage of free nitric acid and total solubilized P_2O_5 in the slurries obtained after acidulating rock phosphate with nitric acid in a nitrophosphate plant.

Studies on Nitric Acidulation of Rock Phosphate: Estimation of Nitric and Phosphoric Acids in the Slurry by High Frequency Titrimetry

By A. D. PANDEY, K. K. MALLICK AND A. K. ROY,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

In the manufacture of nitrophosphate¹⁻³ by the interaction of rock phosphate and nitric acid with or without sulphuric or phosphoric acid, correct reaction conditions have to be strictly maintained in order to ensure maximum recovery of P_2O_5 from the rock. For this purpose, samples of reaction slurry are drawn out at frequent intervals and analysed for their ingredients. In the literature, no quick and accurate method of estimation has been described which can be employed easily for plant control where nitric acid is used for the acidulation. The standard gravimetric and volumetric methods available for estimating the ingredients are time-consuming. Moreover, it is not very clear from the data available so far what are the materials formed when rock is acidulated with different amounts of nitric acid.

The importance of this reaction is increasing due to its utility in the manufacture of nitrophosphates, an important group of fertilizers now manufactured in India and other parts of the world. In India, the Trombay unit of FCI Ltd. has been designed to produce 330,000 tonnes of sulphonitric nitrophosphates of the nominal grade 12.9-12.9.0 and now it is producing phosphonitric nitrophosphate of 20-20-0 grade; besides this plant, other nitrophosphate plants are likely to be set up due to high cost of sulphur which is essential for other phosphatic fertilizers.

In order to get a thorough knowledge of the in-

redients formed by the acidulation of rock phosphate with nitric acid, it was thought desirable to carry out a detailed study of this reaction; for this purpose, it is essential to develop a quick and accurate method for estimation of ingredients present in the slurry after acidulation of the rock.

In this context, high frequency⁵ titrimetry seemed promising as many workers⁶⁻¹⁰ have applied it in the estimation of several acids and bases, in aqueous and nonaqueous media. In several communications¹¹⁻¹⁴ from this laboratory also, this technique has been applied in developing analytical methods in the field of fertilizer technology. Specially in one of the papers¹³, it has been applied in the estimation of phosphate, sulphate and fluosilicate in the wet process phosphoric acid. The present investigation was undertaken to develop a method for quick estimation of nitric and phosphoric acids and also hydrofluosilicic acid, if any, in nitrophosphate slurries.

Experimental

Materials and Apparatus: All the solutions were made in deionized carbon dioxide-free water and the chemicals used were of A. R. or G. R. quality.

The high frequency titrimer used in this investigation is known as oscillotitrator*, developed by E. Pungor⁵.

*Type OK-302 manufactured by Radekisz, Budapest, Hungary.

It operates at a frequency of 140 Mc/s and is used for the measurement of high frequency conductivity where there is no galvanic connection between the measuring system formed by the electrodes and the solution to be tested.

The magnetic vibrating stirrer incorporated in the instrument is a separate unit, which can be taken out or pushed inside the instrument as required.

The cell used is of capacitive measuring type and both the electrodes of the cell are connected through a capacitor to the oscillating circuit. The solution to be titrated is taken in a pyrex glass beaker of 250 ml. capacity and is placed between the two metallic rings forming the two electrodes of the cell; the diameter of the rings is such that they can just fit around the beaker.

The titrimeter is connected to the mains through a voltage stabilizer and the solution to be titrated is continuously stirred with the magnetic stirrer except when the reading is taken. The titrant, 0.1 N caustic soda, is added in 0.5 ml. portions from a 5 ml. microburette having a least count of 0.01 ml. All the titrations are done in very dilute solutions and the total dilution in each case remains the same; 2 to 5 ml. of the stock solutions of the pure acids and of slurries is diluted to 200-225 ml. The change in meter reading of the instrument which follows the change in conductance of the system titrated is plotted against the volume (in ml.) of the titrant added.

Procedure: When rock phosphate was reacted with nitric acid, the acidulate consisted mainly of phosphoric, nitric and hydrofluosilicic acids and calcium nitrate; in addition, some calcium salts, silica and organic matter were also present. In order to have a detailed knowledge of the constituents present in the slurry as also of their amounts, the following systems were titrated (a) nitric acid alone, (b) phosphoric acid alone, (c) hydrofluosilicic acid alone, (d) mixture of phosphoric and nitric acids, (e) mixture of nitric and hydrofluosilicic acids, (f) mixture of phosphoric and hydrofluosilicic acids, (g) mixture of nitric, phosphoric and hydrofluosilicic acids (h) different slurries prepared by the acidulation of rock phosphate with different amounts of nitric acid. The effect of calcium nitrate and monocalcium phosphate on the titration of a mixture of phosphoric acid and nitric acid was also studied.

The different slurries used for titration were obtained by treating 50 g. of Jordan rock phosphate† with different quantities of 53 per cent nitric acid obtained directly

from plant. The acid was heated in a beaker upto 65-70°C and then the rock was slowly added to it in small portions with constant stirring continued till 1 hour after the complete addition of the rock. In all, 9 different slurries, in which the rock to nitric acid ratio was changed from 1:1 to 1:2.6 (by wt), had been prepared.

After preparation of the slurries, a weighted amount (20-25 g.) of each was taken and diluted to 500 ml. for preparation of stock solutions.

In all the titrations, the optimum concentrations of the acids or mixtures that should be taken in the titration cell for the maximum sensitivity of instrument to get sharp breaks in the titration curves were initially determined by trial and error. The stock solutions were prepared by diluting various acids and mixtures to be titrated to known volumes and 1, 2., 2.5 ml. etc. of these were taken in the titration cell to which deionized water was added so that the final volume of the solution in each case remained the same and the level of the solution ready for titration was slightly higher than the upper edge of the upper electrode.

Results and Discussion

The results of high frequency titrimetric determinations of individual acids in dilute solutions are given in Table 1 and titration curves for the individual acids taken in pure form are shown in Fig. 1. It is seen from the curve-I (Fig. 1) that in the case of nitric acid, only one break occurred on the complete neutralization of the acid; with hydrofluosilicic acid two breaks occurred corresponding to NaHSiF_6 and Na_2SiF_6 for the pure acid in very dilute solution but when the acid concentration increased only one break was obtained, indicating thereby the complete neutralization of the acid.

The results of titration of phosphoric acid against 0.1N caustic soda in dilute solution showed three breaks (curve-III, Fig. 1) corresponding to neutralization of this acid to mono-, di- and tri-sodium phosphates. But when the acid concentration was higher, only first two breaks or in some cases only first break occurred. Estimation of these acids in dilute solutions showed that the error does not exceed 2.5 per cent (Table 1).

In Fig. 2 are shown the titration curves of mixtures of (1) hydrofluosilicic and nitric acids (2) hydrofluosilicic and phosphoric acids and (3) nitric and phosphoric acid. In curve I (Fig. 2) the first break corresponds to the half neutralization of hydrofluosilicic acid, i.e. from H_2SiF_6 to NaHSiF_6 ; the second break corresponds to the complete neutralization of nitric acid and the remaining hydrofluosilicic acid together. The curve-II (Fig. 2) shows

† Its P_2O_5 content = 30.04 per cent and CaO = 47.9 per cent.

TABLE 1—HIGH FREQUENCY TITRATION OF NITRIC, HYDROFLUOSILICIC AND PHOSPHORIC ACIDS
TAKEN SEPARATELY AGAINST STANDARD CAUSTIC SODA

HNO ₃ as N					H ₂ SiF ₆ as F				H ₃ PO ₄ as P ₂ O ₅			
	Taken, mg.	Found, mg.	Error, %	Std. Deviation	Taken, mg.	Found, mg.	Error, %	Std. Deviation	Taken, mg.	Found, mg.	Error, %	Std. Deviation
1. (a)	1.398	1.421	1.76	—	5.664	5.724	1.08	—	7.080	7.034	0.59	—
(b)	1.398	1.416	1.38	—	5.664	5.710	0.82	—	7.080	7.048	0.45	—
(c)	1.398	1.419	1.50	—	5.664	5.654	0.18	—	7.080	7.021	0.84	—
	—	—	—	0.012	—	—	—	0.033	—	—	—	0.024
(d)	1.398	1.395	0.21	—	5.664	5.728	1.14	—	7.080	7.064	0.23	—
(e)	1.398	1.400	0.14	—	5.664	5.669	0.09	—	7.080	7.095	0.21	—
2. (a)	2.098	2.108	1.43	—	8.496	8.609	1.33	—	10.620	10.739	1.12	—
(b)	2.098	2.128	1.98	—	8.496	8.598	1.20	—	10.620	10.715	0.90	—
3. (a)	2.796	2.862	2.50	—	11.328	11.498	1.50	—	14.160	14.350	1.50	—
(b)	2.796	2.852	2.01	—	11.328	11.554	1.98	—	14.160	14.325	1.16	—

the neutralization of a mixture of hydrofluosilicic and phosphoric acids; here hydrofluosilicic acid shows only one break at its complete neutralization point corresponding to the first break in the curve which may be due to increase in total hydrogen ions present in the titrating solution. The second break corresponds to one-third

neutralization of phosphoric acid and is followed by the second and third neutralization points of phosphoric acid. Curve-III (Fig. 2) is the high frequency titrimetric graph of a mixture of phosphoric and nitric acids which is most important so far as nitric acidulation of rock phos-

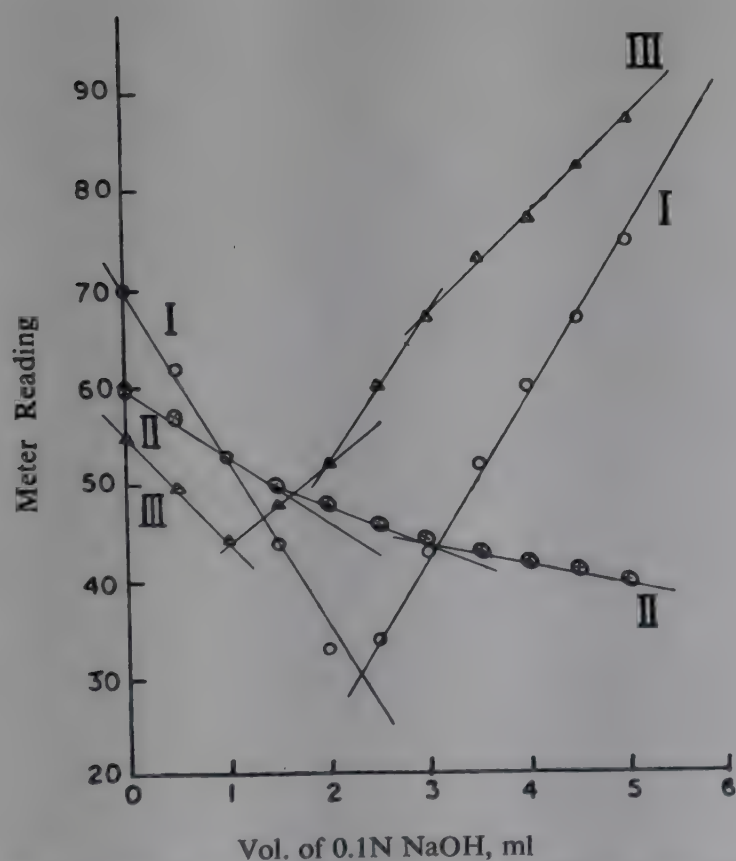


Fig. 1—High Frequency Titration of Acids Taken Separately
No. I—2.5 cc. HNO₃
No. II—3 cc. H₂SiF₆
No. III—3 cc. H₃PO₄

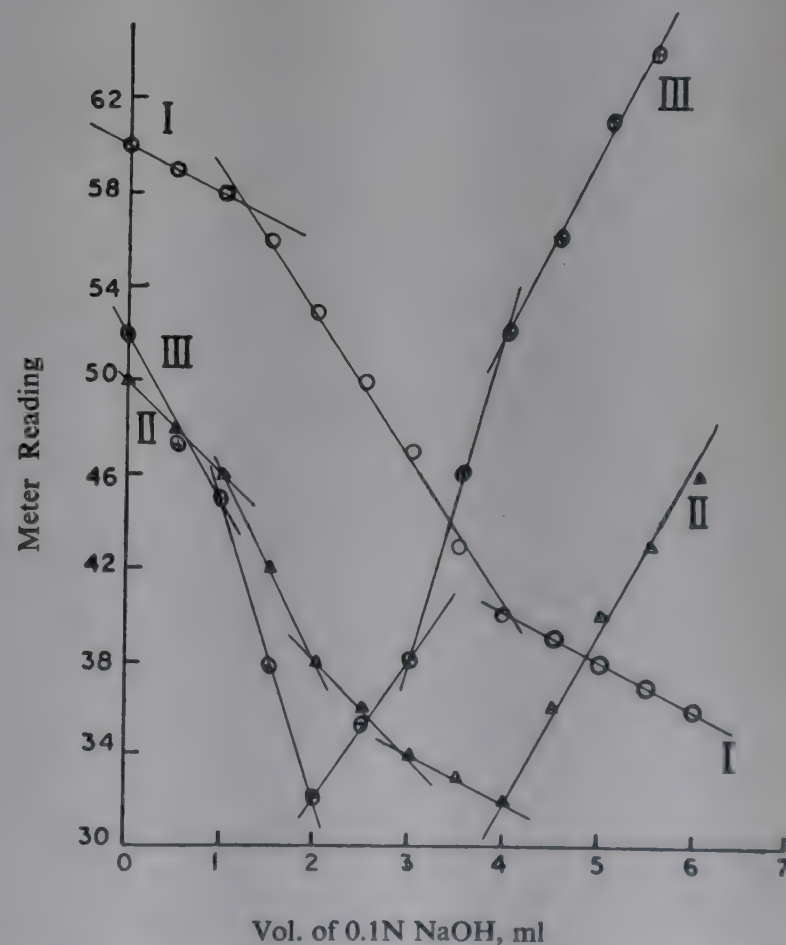


Fig. 2—High Frequency Titration of Acids Taken Two at a Time
No. I—2 cc. 0.1 N H₂SiF₆ + 2 cc. 0.1 N HNO₃
No. II—1 cc. 0.1 N H₂SiF₆ + 3 cc. 0.1 N H₃PO₄
No. III—1 cc. 0.1 N HNO₃ + 3 cc. 0.1 N H₃PO₄

phate is concerned. It is seen from the curve that the first break in the graph corresponds to the complete neutralization of nitric acid and the second to one-third neutralization of phosphoric acid; the third and fourth breaks are due to the second and third neutralization points of phosphoric acid. The results of the titration of these acids taken two at a time are given in Table 2. It is seen (Table 2) that this technique gives reasonably accurate results of individual acids present in the mixture; the error did not exceed 2.5 per cent in any case.

When a mixture of hydrofluosilicic, nitric and phosphoric acids were titrated against caustic soda, the first break (curve-III, Fig. 3) corresponds to complete neutralization of hydrofluosilicic acid as concentration of hydrogen ion present in the solution is more; the second break corresponds to the complete neutralization of nitric acid and third to one-third neutralization of phosphoric acid; the last two breaks in the curve correspond to the second and third neutralization points of phosphoric acid. The error in the estimation of the three acids in the same solution was within 2.5 per cent in the concentration ranges studied (Table 3). Sharp breaks are obtained in all the titration curves corresponding to mixtures of acids mentioned above.

In Table 4 and Fig. 3, the results of titration of mixture

of nitric and phosphoric acids with different amounts of calcium nitrate are given. It is seen that there is a slight change in the nature of curves in the presence of calcium nitrate; the nitric acid portion of the curve become flattened and at higher concentrations of calcium nitrate

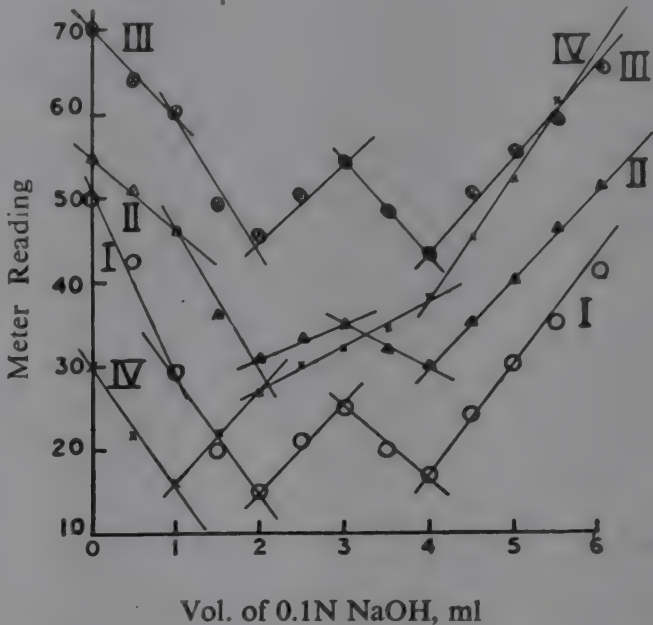


Fig. 3—Effect of $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ on the estimation H_3PO_4 and HNO_3
 No. I—1 cc. HNO_3 + 3 cc. H_3PO_4 + 1 cc. 0.1 M $\text{Ca}(\text{NO}_3)_2$
 No. II—1 cc. HNO_3 + 3 cc. H_3PO_4 + 2 cc. 0.1 M $\text{Ca}(\text{NO}_3)_2$
 No. III—1 cc. HNO_3 + 3 cc. H_3PO_4 + 4 cc. 0.1 M $\text{Ca}(\text{NO}_3)_2$
 No. IV—3 cc. H_3PO_4 + 5 cc. 0.1 M $\text{Ca}(\text{H}_2\text{PO}_4)_2$

TABLE 2—HIGH FREQUENCY TITRATION OF MIXTURES OF NITRIC, HYDROFLOUSILICIC AND PHOSPHORIC ACIDS TAKEN TWO AT A TIME AGAINST STANDARD CAUSTIC SODA

Mixture HNO_3 + H_2SiF_6								
Nos.	Taken, mg.		Found, mg.		Error, %		Standard Deviation	
	HNO_3 as N	H_2SiF_6 as F	HNO_3 as N	H_2SiF_6 as F	HNO_3	H_2SiF_6	HNO_3	H_2SiF_6
	1	2	3	4	5	6	7	8
1. (a)	1.398	5.664	1.410	5.720	0.86	0.98	—	—
(b)	1.398	5.664	1.390	5.710	0.57	0.80	—	—
(c)	1.398	5.664	1.425	5.660	1.93	0.070	—	—
							0.027	—
(d)	1.398	5.664	1.420	5.680	1.57	0.28	—	0.025
(e)	1.398	5.664	1.395	5.675	0.21	0.19	—	—
2.	1.398	11.328	1.420	11.495	1.57	0.59	—	—
3.	2.098	11.328	2.130	11.550	1.52	1.96	—	—
4.	2.796	5.664	2.865	5.710	2.46	0.82	—	—
5.	2.796	8.496	2.850	8.595	1.92	1.19	—	—

[Contd.]

TABLE 2 (Contd.)—HIGH FREQUENCY TITRATION OF MIXTURES OF NITRIC, HYDROFLOUSILICIC AND PHOSPHORIC ACIDS TAKEN TWO AT A TIME AGAINST STANDARD CAUSTIC SODA

Mixture $\text{HNO}_3 + \text{H}_3\text{PO}_4$							
Taken, mg.		Found, mg.		Error, %		Standard Deviation	
HNO_3 as N	H_3PO_4 as P_2O_5	HNO_3 as N	H_3PO_4 as P_2O_5	HNO_3	H_3PO_4	HNO_3	H_3PO_4
9	10	11	12	13	14	15	16
1.398	7.080	1.430	7.205	2.28	1.78	—	—
1.398	7.080	1.390	7.105	0.57	0.35	—	—
1.398	7.080	1.395	7.100	0.21	0.28	—	—
						0.018	—
							0.050
1.398	7.080	1.425	7.150	1.92	1.00	—	—
1.398	7.080	1.415	7.200	1.21	0.17	—	—
1.398	1.620	1.425	10.740	1.92	1.13	—	—
2.088	14.160	2.110	14.250	0.57	0.63	—	—
2.796	7.080	2.840	7.120	1.57	0.56	—	—
2.796	14.160	2.845	14.350	1.75	1.34	—	—
Mixture $\text{H}_2\text{SiF}_6 + \text{H}_3\text{PO}_4$							
Taken, mg.		Found, mg.		Error, %		Standard Deviation	
H_2SiF_6 as F	H_3PO_4 as P_2O_5	H_2SiF_6 as F	H_3PO_4 as P_2O_5	H_2SiF_6	H_3PO_4	H_2SiF_6	H_3PO_4
17	18	19	20	21	22	23	24
5.664	7.080	5.680	7.005	0.28	0.10	—	—
5.664	7.080	5.729	7.205	1.00	1.78	—	—
5.664	7.080	5.700	7.150	0.64	1.00	0.026	—
							0.075
5.664	7.080	5.669	7.105	0.07	0.03	—	—
5.664	7.080	5.710	7.150	0.82	1.00	—	—
11.328	7.080	11.540	7.125	1.87	0.63	—	—
11.328	1.620	11.550	10.745	1.96	1.18	—	—
8.496	14.160	8.550	14.200	0.62	0.28	—	—
5.664	14.160	5.720	14.210	1.00	0.35	—	—

TABLE 3—HIGH FREQUENCY TITRATION OF MIXTURES OF NITRIC, HYDROFLOUSILICIC AND PHOSPHORIC ACIDS

Nos.	HNO ₃ in the Mixture as N			H ₂ SiF ₆ in the Mixture as F			H ₃ PO ₄ in the Mixture as P ₂ O ₅		
	Taken, mg.	Found, mg.	Error, %	Taken, mg.	Found, mg.	Error, %	Taken, mg.	Found, mg.	Error, %
1.	1.398	1.420	1.57	5.664	5.740	1.40	7.080	7.200	1.70
2.	1.398	1.425	1.93	11.328	11.450	1.08	7.080	7.150	1.00
3.	2.098	2.138	1.98	8.496	8.598	1.20	10.620	10.730	1.38
4.	2.796	2.850	1.85	5.664	5.750	1.53	14.160	14.435	1.93

TABLE 4—HIGH FREQUENCY TITRATION OF NITRIC AND PHOSPHORIC ACIDS IN PRESENCE OF Ca(NO₃)₂ AND Ca(H₂PO₄)₂ SOLUTIONS

Nos.	Ca(NO ₃) ₂ , mg.	Ca(H ₂ PO ₄) ₂ , mg.	HNO ₃ as N			H ₃ PO ₄ as P ₂ O ₅		
			Taken, mg.	Found, mg.	Error, %	Taken, mg.	Found, mg.	Error, %
1.	16.400	—	1.398	1.415	1.21	7.080	7.200	1.71
2.	32.800	—	1.398	1.425	1.92	7.080	7.230	2.10
3.	49.200	—	1.398	1.420	1.57	7.080	7.250	2.39
4.	65.600	—	1.398	1.430	2.28	7.080	7.240	2.25
*5.	—	12.852	—	—	—	7.080	7.200	1.71
*6.	—	25.704	—	—	—	7.080	7.225	2.04

*In the presence of Nitric acid monocalcium phosphate will not exist.

present in the titrating solution the error also increases. But the error does not exceed 2.5 per cent upto a concentration of 65.6 mg. of calcium nitrate in the titrating solution. The effect of monocalcium phosphate on the estimation of phosphoric acid alone has been studied and it has been found that the presence of monocalcium phosphate upto 25.7 mg. has got no adverse effect on the estimation and monocalcium phosphate gives its own separate curve after second break of phosphoric acid present (Table 4, Fig. 3).

In Table 5 and Fig. 4 are given the results with different slurries obtained by the nitric acidulation of rock phosphate. The slurries studied had different rock/acid ratio. In some cases, the amount of acid is less than that required for complete reaction with the rock; in others, it is in excess. It is found that when rock/acid ratio lies between 1:2.2 to 1:2.3, complete reaction of rock takes place. When nitric acid remained in excess it gave its separate curve and can be determined easily. Curve-II (Fig. 3) indicates a slurry in which nitric acid is in excess (rock/acid ratio is 1:2.6); here the first break in the curve showed complete neutralization of excess nitric acid; the second is that of one-third of phosphoric acid and third and fourth breaks were also due to phosphoric acid present in it. The curve-I (Fig. 3) corresponds to the slurry in which the quantity of nitric acid is less than that required for complete reaction of rock phosphate present

(rock/acid ratio 1:1.6). In this curve, the first break is due to one-third neutralization of phosphoric acid

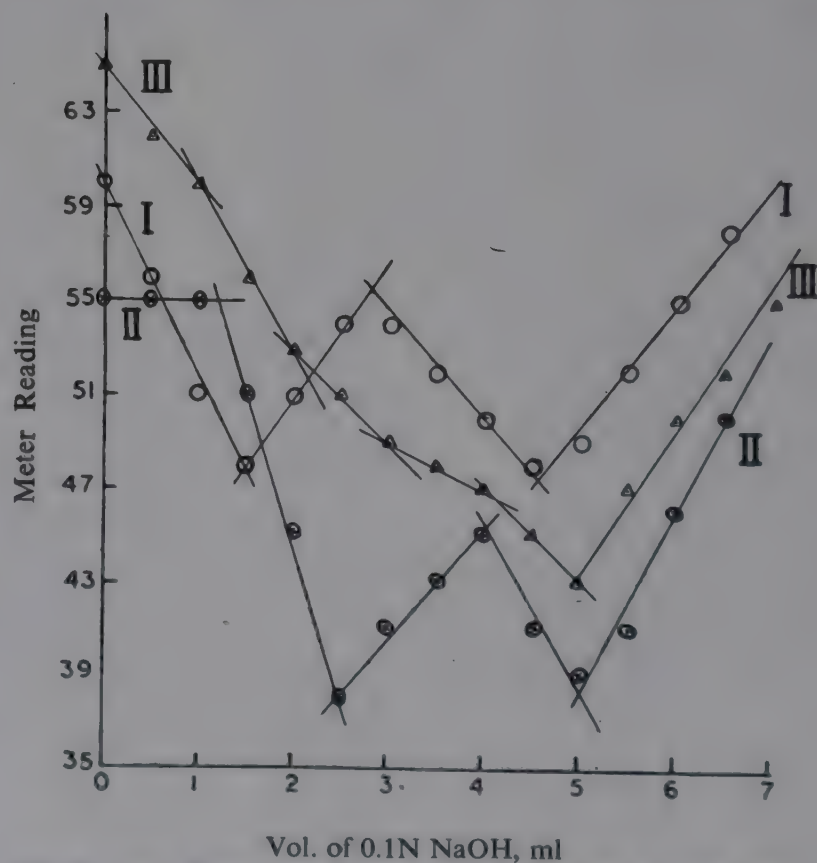


Fig. 4—High Frequency Titration of Acidulation Rock Phosphate against 0.1N NaOH

No. I—Rock Vs Nitric Acid 1: 1.6
No. II— 1: 1.6
No. III—1 cc. H₂SiF₆ + 1 cc. HNO₃ + 3 cc. H₃PO₄ against 0.1N

TABLE 5—HIGH FREQUENCY TITRATION OF NITRIC PHOSPHATE SLURRY WITH STANDARD CAUSTIC SODA

Sample Nos.	Rock:	Per 100 g. Rock			
	Plant	Standard Method		Oscillometric Titration	
	Nitric acid	H ₃ PO ₄ as P ₂ O ₅	Ca as CaO	H ₃ PO ₄ as P ₂ O ₅	Error, %
1	1:1	13.800	27.098	14.160	2.60
2	1:1.2	15.180	33.488	15.576	2.62
3	1:1.4	16.590	37.282	16.992	2.43
2	1:1.6	19.350	40.275	19.882	2.75
5	1:1.8	22.038	41.636	22.464	2.13
6	1:2.0	24.256	42.504	24.712	2.62
7	1:2.2	25.750	45.725	25.998	1.14
8	1:2.4	28.985	47.334	29.554	1.96
9	1:2.6	29.440	47.522	30.042	2.04

formed and the second and third breaks also due to the same acid. No other breaks were obtained in curves-I and II (Fig. 3) which indicate that whether nitric acid was in excess or in insufficient amount, only phosphoric acid was formed as the water-soluble component when the former reacted with rock. The formation of mono-calcium phosphate is not observed even when the amount of nitric acid was insufficient for complete reaction with rock phosphate. The results (Table 5) clearly show the variation of P₂O₅ and calcium present in soluble form in different slurries prepared. The P₂O₅ and calcium content of the slurries go on increasing with the increase of rock/acid ratio. After complete reaction, these values become constant. The error in the values of P₂O₅ determined by high frequency method as compared to the standard method does not exceed 3 per cent in any case. The values of excess nitric acid, if any, are also obtained from the first break in the titration curves, as already indicated.

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Electrode potentials in sodium chloride solution (3 g/100 ml) of mild steel panels coated with different primers and top coats have been measured and compared with results of corrosion cabinet tests and exposure tests in an ammonium sulphate plant. Some correlation has been noted among the results of three sets of experiments.

Some Studies on the Evaluation of Protective Coatings By Electrode Potential Measurements

By H. D. SARKAR AND A. K. ROY,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

In previous communications^{1,2} results were reported on some laboratory and field experiments to assess the performance of some protective coatings for use in fertilizer plant location. Resistance measurements were utilized to predict the performance of some primers. In the present communication attempts have been made to utilize electrode potential measurements of mild steel panels coated with different primers and top coats for evaluating their performance. Corrosion cabinet tests and field exposure tests with the coated panels have also been performed and the results compared with the electrode potential values.

Experimental

Mild steel panels were cut out and cleaned by dilute sulphuric acid at 60°C. They were then washed in water and phosphate/chromate treatment was given to them. The panels were next dried.

To a batch of these panels, one coat each of five primer paints, viz. (i) Zinc chromate/red oxide, (ii) Grey and (iii) Zinc chromate all in chlorinated rubber base and also (iv) Grey and (v) red oxide/zinc chromate both in alkyd base, were applied by brush; the panels were then allowed to dry for seven days. Electrode potential measurements were carried out with the dried panels; corrosion cabinet tests were also performed with them.

To a further batch of panels one coat of red oxide/zinc chromate primer* was applied. After they were dried, four sets of eight panels were taken from this lot and separately one top coat of the following was applied to

each set: (1) alkyd grey enamel (2) chlorinated rubber cream (3) phenolic based bituminous black developed in this laboratory and (4) a commercial sample of bituminous black. The panels were then dried under laboratory conditions for seven days.

For electrode potential measurements, panels were of size 2.5 × 15 cm and for corrosion cabinet and exposure tests, they were of the size 7.5 × 15 cm. The thickness of the dried film was measured before starting the experiment.

The different primers and top coats used in these studies are described below:

Primer No.	1	2	3	4	5
Resin	18.0	18.0	18.5	22.5	20.0
Red oxide	25.0	—	—	—	22.0
TiO ₂	—	25.5	—	22.5	—
ZnO	—	9.5	—	9.0	—
L. Black	—	0.7	—	0.6	—
Zn chrome	8.2	—	28.5	—	8.2
Barytes	12.5	12.0	16.5	16.5	16.5
Solvent	30.5	32.0	30.0	32.0	30.5
Drier	0.0	0.0	0.0	0.90	0.90

Top coat Enamel No	1	2	3	4
Resin	40.5	39.5	25.0	21.5
TiO ₂	10.0	10.0	—	—
ZnO	3.5	3.2	—	—
C. Black	0.3	—	—	—
Yellow chrome	—	1.0	—	—
Talc	3.0	2.5	—	5.2
Bitumin	—	—	27.5	23.5
Solvent	30.0	30.5	40.5	42.5
Drier	1.0	0.8	0.9	0.9

*I.S. Specification 2074

Electrode Potential Measurements: Electrode potential measurements were carried out with mild steel panels coated with primers alone as also with those treated with both primers and top coats. One inch of the panel at the top was not given any protection. The sides and the bottom of the coated panels were further treated with paraffin before the experiments were started.

The experiments were carried out in sodium chloride solution (3 g./100 ml) at 40°C., The panels were partially immersed in the salt solutions in the beaker so that the upper portions of the panels remained above the liquid level; different beakers were used for different panels. The electrode potential of the panel was measured with reference to a saturated calomel electrode with the help of Fischer Automatic Titrator (Model MS 2). The salt solution in which a panel was immersed was in connection with sodium chloride solution (3 g./100 ml) kept in another beaker by means of a moistened filter paper strip, and the solution in the later beaker was connected by means of another moistened filter paper strip with saturated potassium chloride solution in a beaker into which the calomel electrode was placed.

Initial potential readings were taken immediately after immersion of the panels in the salt solution. For the panels coated with primers only, the interval between the first and second readings was 8 hr; thereafter, readings were taken at 24 hr. intervals (Fig. 1). For the panels having both primers and finishing coats, readings were taken at '24 hours' intervals; however, in Fig. 2

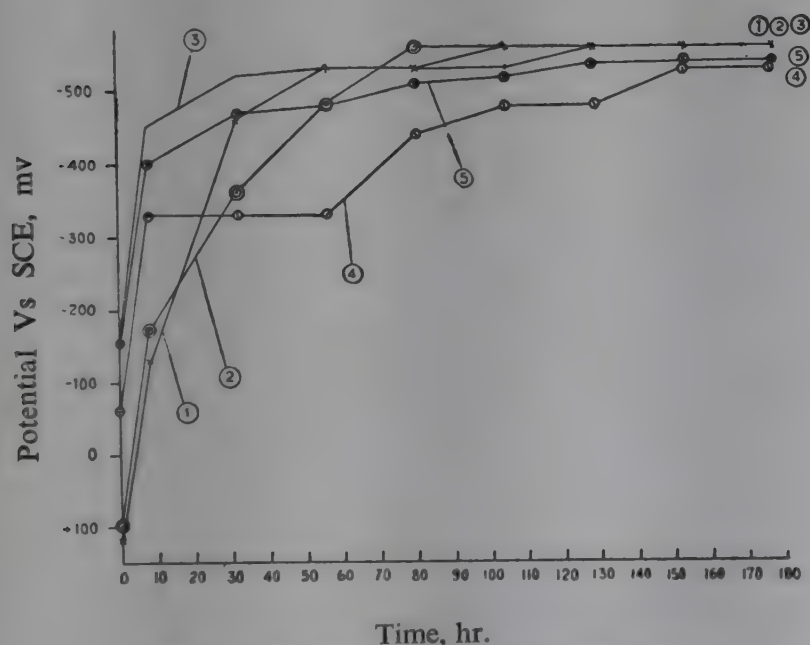


Fig. 1—Electrode Potential of Coated Panels

1. Chlorinated Rubber Zinc Chromate Primer
2. Chlorinated Rubber Grey Primer
3. Chlorinated Rubber Red Oxide/Zinc Chromate Primer
4. Alkyl based Group Primer
5. Alkyl based Red Oxide/Zinc Chromate

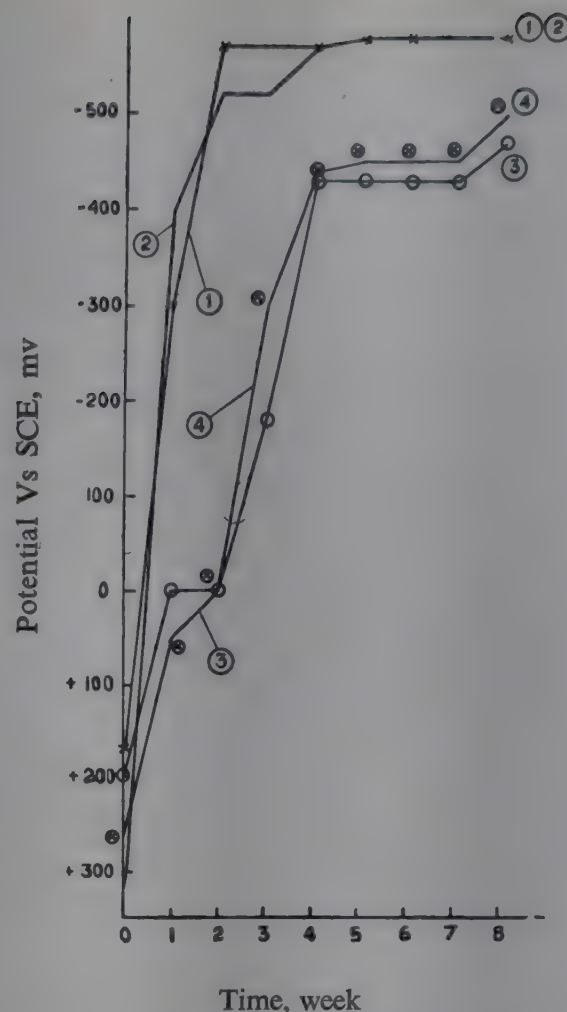


Fig. 2—Electrode Potential of Panels with Primers and Top Coats

1. Alkyl based Grey
2. Chlorinated Rubber Cream
3. Phenolic Bituminous Cream
4. Bituminous Black

average values for a period of one week have been given. Visual observations were also recorded along with the potential readings.

Corrosion Cabinet Test: Panels were prepared and coated with different types of primers and with primer and top coats according to the same procedure as followed in case of electrode potential measurements. They were then tested in corrosion cabinet according to Indian standard specification** for seven days and the observations recorded (Tables 1 and 3).

Exposure Test at Plant Site: Method of panel preparation and application of primer and top coat was the same as in the case of corrosion cabinet tests; the different coated panels were dried for seven days and then placed on the structure of the conveyor belt in the ammonium sulphate plant at Sindri where an almost continuous spillage of ammonium sulphate dust takes place. The first inspection of the panels was made after one month and subsequently after three months intervals. Any deterioration of the coating such as loss in gloss, blistering, checking, cracking and rusting was

** I.S.: 101-1964

TABLE 1—RESULTS OF CORROSION CABINET TESTS WITH PRIMERS

No.	Primers	Average film thickness, mils	After 24 hr.	After 48 hr.	After 72 hr.	After 96 hr.	After 120 hr.	After 144 hr.	After 168 hr.
1.	Chlorinated rubber-based red oxide	1.5	Pin point corrosion at two places	Same as before	Same as at 48 hr.	More sign of corrosion at places with small blister	Same as at 96 hr.	Blistering effect becomes more pronounced	Condition remains as before
2.	Chlorinated rubber-based grey	1.5	Sign of corrosion at places	Same as before	Same as at 48 hr.	More sign of Corrosion at several places	Same as at 96 hr.	A few blisters in addition	Conditions remains same as before
3.	Chlorinated rubber-based Zinc chrome	2.0	Defect not noticeable	Minute blisters at places	More blister	Pin point corrosion at places of blisters	Previous effect becomes more	Same as at 120 hr.	Corrosion and blisters at several places
4.	Alkyd-based grey	1.5	Film becomes whitish	Same as before	Same as at 48 hr.	A few minute blisters	Blisters become more at more places	Pin point corrosion at places of blisters	More pin point corrosion
5.	Alkyd-based red oxide	1.5	Defect not noticeable	No appreciable change	Same as at 48 hr.		Minute sporadic blisters	Small blisters throughout the panel	Pin point corrosion at places with blisters

TABLE 2—OBSERVATION ON THE PANELS WITH PRIMERS IN IMMERSSED CONDITION DURING THE POTENTIAL MEASUREMENT

Primers	After 24 hr.	After 48 hr.	After 72 hr.	After 96 hr.	After 120 hr.	After 144 hr.	After 168 hr.
Chlorinated rubber-based red oxide	Pin point corrosion at two places	Same as before	No change	More corrosion at places with blisters	Previous effect becomes more	Severe corrosion at the immersed portion	
Chlorinated rubber-based grey	Pin point corrosion on both sides of the panel at places	More sign of corrosion	Condition remains same during the period				
Chlorinated rubber-based Zinc chrome	Defect not noticeable during the period				Pin point corrosion at three places	Sign of corrosion becomes more at places during the period	
Alkyd-based red oxide	Defect not noticeable during the period				Small sporadic blisters	Sign of corrosion at the place of blisters	Previous effect becomes more
Alkyd-based grey	Defect not noticeable during the period				Pin-point corrosion at places	Corrosion with blisters at places	More corrosion at places

noted (Table 4). The exposure test was conducted for eighteen months.

Results and Discussion

Electrode potentials of painted specimens of steel in salt solutions have been used earlier^{3,4} in assessing the performance of the protective coatings. In general, the

more positive the potential the better is the performance of the painted panel in service.

It will be seen from the results of the electrode potential measurements (Fig. 1) that at the initial stage, panels coated with chlorinated rubber-based Zinc chromate and grey primers started with positive potentials (Fig. 1, curves 1 and 2) but soon after, the potential values

TABLE 3—RESULTS OF CORROSION CABINET TESTS WITH RED OXIDE ZINC CHROMATE PRIMER AND DIFFERENT TOP COATS

No.	Top Coats	Average Film thickness, mils	After 24 hr.	After 48 hr.	After 72 hr.	After 96 hr.	After 120 hr.	After 144 hr.	After 168 hr.
1.	Enamel grey alkyd-based	2.5	Appreciable loss in gloss	Minute blisters at one place	Same as at 48 hr.	More blisters along with previous one	Condition remains almost same		The film becomes whitish
2.	Cream chlorinated rubber-based	2.5	Defect not noticeable	Minute blisters packed at places	Condition remains same	More minute blisters throughout the panel	Previous effect becomes more		Brown spot at places.
3.	Phenolic bituminous black	3.0	Defect not noticeable	Condition remains almost same during the period					
4.	Bituminous black	3.0	Defect not noticeable	Condition remains almost same during the period					

TABLE 4 OBSERVATION ON THE PANELS WITH PRIMERS AND TOP COATS EXPOSED AT THE PLANT SITE

Top Coats	After 1 month	After 3 months	After 6 months	After 9 months	After 12 months	After 15 months	After 18 months
Enamel grey alkyd-based	Appreciable loss in gloss	No defect noticeable during the period			Checking at places and film becomes whitish	More checking with cracking at places	More cracking
Cream; chlorinated rubber-based	Appreciable loss in gloss	Same as before	Sign of corrosion at one place, with blisters at places	Checking at places along with previous effect	More checking with blisters	Severe cracking throughout the panel	Discontinued
Phenolic-base bituminous black	No change	Same as before	loss in gloss	Previous effect becomes more pronounced	Brown spot at one place	Brown spot becomes larger	Same as seen after 15 months
Bituminous black	No change	Same as before	Appreciable loss in gloss	Condition remains same as at six months	Pin point corrosion at places	Previous effect becomes slightly more	More corrosion at places

TABLE 5—OBSERVATION ON PANELS WITH RED OXIDE/ZINC CHROMATE PRIMERS & TOP COATS IN IMMERSED CONDITION DURING POTENTIAL MEASUREMENT

Top coats	1st week	2nd week	3rd week	4th week	5th week	6th week	7th week
Enamel grey alkyd-based	Very minute blisters at places	Condition remains almost same	Brown spots at few places	Same as at 3rd week	Brown spots at almost throughout the panel		
Cream/chlorinated rubber based	Brown spot at one place	Same as at 1st week	Minute blisters at several places	Brown spots at the place of blisters	Previous effect become more		Corrosion throughout the immersed portion
Phenolic-based bituminous black	No defect noticeable	Condition remains same as before			A few blisters at places	More blisters at places	
Bituminous black	No defect noticeable	Condition remains same as before			No appreciable change except loss in gloss	The film becomes soft at places	

rapidly went on assuming more and more negative values and reached the maximum negative values of the order of -550 to -570 mv with respect to saturated calomel electrode after about 96 hr. The electrode potential of the panel coated with chlorinated rubber-based red oxide primer (Fig. 1, curve 3) started with a negative value, became progressively more and more negative in the same manner as in the case of the previous two panels and also reached a maximum negative value of about -560 mv after about 96 hr.

The panels coated with alkyd based red oxide and grey primers started with negative potentials (Fig. 1, curves 4 and 5) but the rate of change in potential to more negative values was appreciably slower than in the case of chlorinated rubber-based primers. These results indicated the superiority of alkyd based primers over chlorinated rubber based ones and also found support from visual observation (Table 2) on the progressive deterioration of the panels. Corrosion cabinet tests (Table 1) also showed the better performance of alkyd based primers as compared to the chlorinated rubber based ones. Thus, in this case, the electrode potential values could be correlated with results of corrosion cabinet tests.

Electrode potential measurements of panels with primer and top coat are shown in Fig. 2. Panels with following two-coat systems were tested.

1. Alkyd-based grey
2. Chlorinated rubber-based cream
3. Phenolic-based bituminous black
4. Bituminous Black

All the panels started with positive potential values. In cases of panels coated with systems (1) and (2) (Fig. 2, curves 1 & 2) change to more negative potential values was considerably more rapid than in the case of panels coated with bituminous black—systems (3) and (4) (Fig. 2, curves 3 and 4). The potential of panels coated with bituminous black remained positive for a week and thereafter the potential assumed progressively negative values with time. The maximum negative values of potential was attained after about seven weeks in all the cases. These results indicate that the panels coated with bituminous black have better performance than others; this inference agrees with the visual observation (Table 5) extended over weeks. The results of corrosion cabinet tests (Table 3) extended over 7 weeks also show that panels coated with two separate bituminous black systems have better performance than those coated with alkyd-based grey or chlorinated rubber-based cream. Thus, the corrosion cabinet tests can be correlated with electrode potential measurements. These results are also, in general, agreement with these of exposure tests (Table 4) carried out for a period of eighteen months in the ammonium sulphate plant at Sindri.

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A low chromium-manganese-molybdenum steel with 0.37 per cent carbon has been studied by electron microscopy, x-ray diffraction and hardness measurements. The studies reveal that the supersaturated ferrite phase, obtained by hardening, transform to lower bainite, upper bainite and ferrite-carbide phases at tempering temperatures corresponding to those of their isothermal transformations with precipitation of $M_{23}C_6$ -type carbide throughout all transformations. The peculiarity of precipitation of $M_{23}C_6$ has been explained as due to retention of such structural nuclei by quenching and further growth of these while tempering. The lattice strain, induced by tempering, is successively decreased with increase in temperature and is totally eliminated after tempering at 650°C.

Tempering Characteristics of a Low Alloy Steel

By C. ARAVINDAKSHAN, A. SEN GUPTA
AND C. V. SRINIVASAN,*

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Alloy steel finds many applications in the modern fertilizer industry. As such, a knowledge of different properties of steel is very essential for proper selection of the material of construction for a particular use. Though extensive work has been done on changes in properties of iron by introduction of alloying elements, it is found that the properties of an alloy steel is not exactly the same which could be expected by the addition of separate elements. Therefore, alloy steels require a thorough study for their properties before they are put in for a particular use.

In this paper, an attempt has been made to study the changes in characteristic, like metallographic structure, hardness, crystalline phase composition, changes in lattice parameter and lattice strain, and nature of carbides present in a hardened commercial low alloy steel after tempering at different temperatures.

Experimental

The experimental samples were prepared in the form of square pieces of about 1 cm. length and breadth and 2 mm. thickness from a commercial low alloy plate having the following approximate composition (per cent): Cr 2, Mn 0.5, Mo 0.25 and C 0.37. These pieces were heated at 900°C for about 30 min. and then suddenly quenched in transformer oil (grade, Shell Oil C). Subsequent tempering was carried out at 150°, 250°, 350°, 450°, 550° and 650°C for about an hour.

After the above heat-treatments, each set of samples was subjected to the following studies: (1) optical and

electron metallographic examination; (2) x-ray diffraction analysis and (3) hardness measurements. The sample pieces were successively polished and then etched in a 2 per cent nital solution for optical metallographic examination. Subsequently, the carbon extraction replicas of the surfaces were stripped off in a 10 per cent nital solution¹. The same experimental pieces were used for x-ray back reflection studies, hardness measurements and carbide extraction.

For accurate lattice parameter calculation of α -Fe phase by x-ray back reflection method, a standard x-ray pattern of powdered α -Fe₂O₃ was superimposed for each exposure of experimental alloy sample. The 'd' value of overlapping reflections 232 and 318 of α -Fe₂O₃² was used to correct the 'd' value of 220 reflection of α -Fe from which the lattice parameter values were calculated. This procedure was meant to eliminate any error that were likely to be introduced by shift in specimen to film distance and film shrinkage during processing. The FeK α (filtered) radiation was used to obtain x-ray back reflection photographs.

For obtaining carbides, the experimental pieces were treated with *aqua regia* and the insoluble products were filtered, washed and dried. The powder method of x-ray analysis was used for the identification of the carbide phases. Prior to extraction of carbides, the hardness number of heat-treated samples were estimated by a Brinell hardness tester.

* Present address : Madras Fertilizers Ltd., Manali, Madras

Results

(i) *Metallographic Analysis*: The optical micrographs did not give much information and therefore have not been included here. The electron-micrographs of the heat-treated steels are reproduced in Fig. 1. The electron-metallograph of hardened low alloy steel showed a ferrite-carbide matrix. When the hardened alloy was tempered at 150°C, the electron micrograph showed a diffused appearance with fine carbide precipitation. The fine carbide precipitation appears to be assemblages of short and thin platelets. The microstructure of the hardened steel tempered at 250°C was slightly different from the previous one. The formation of ferrite needles containing long carbide platelets in parallel array was clearly shown. These long carbide platelets make an angle of about 60° with respect to a common axis. A tempering at 350°C of the hardened alloy showed intense precipitation of carbide in the micro-structure. The mode of carbide precipitation no longer follows the pattern of the one tempered at 250°C. The carbides took the form of unresolved stringers without any special orientation to each other. There were also evidence of fine carbides resembling those found in pearlitic structures. The micrograph of the sample tempered at 450°C showed only normal structure of ferrite and carbides. The tendency of coarsening in the carbide particles were seen. When it was tempered at 550°C, the precipitation and coarsening were intense; there was tendency of spheroidization and globular type carbide formation. The carbide precipitation appeared more or less complete. The sample tempered at 650°C showed a completely different micrograph; it indicated the formation of polygonal ferrite.

(ii) *X-Ray Diffraction Analysis*: The back reflection photographs of all polished and etched samples showed only the crystalline phase of α -Fe (Fig. 2). However, there were significant changes in the 220 reflection of α -Fe structure from sample to sample.

The 220 reflection of the hardened sample showed well resolved doublet α_1 , and α_2 of the FeK α radiation. When this sample was tempered at 150°C, the sharpness and resolution of the doublet were lost and the 220 reflection became diffuse and broad. A further increase in the tempering temperature gradually decreased the broadening and diffused appearance of the 220 reflection. Finally, tempering at 650°C restored the sharpness and resolution of the doublet of 220 reflection.

An accurate lattice parameter calculation for the α -structure (Table 1) using its corrected 220 reflection shows that the hardened alloy has its value ($a=2.8692$ Å) very near to that of pure iron lattice ($a=2.8663$ Å). On

TABLE 1—LATTICE PARAMETER AND HARDNESS VALUES FOR HEAT-TREATED LOW ALLOY STEEL SAMPLES

Sl. No.	Sample	Lattice Parameter of Structure (a), Å	Hardness Number, Bhn
1.	900°C (Heated and quenched)	2.8692	464
2.	150°C (tempered)	2.8745	483
3.	250°C (")	2.8745	442
4.	350°C (")	2.8743	349
5.	450°C (")	2.8743	349
6.	550°C (")	2.8734	347
7.	650°C (")	2.8734	145
8.	Pure α -Fe*	2.8663	—

*From *X-ray Metallography* by A. Taylor (John Wiley & Sons Inc., New York), 1961, 964.

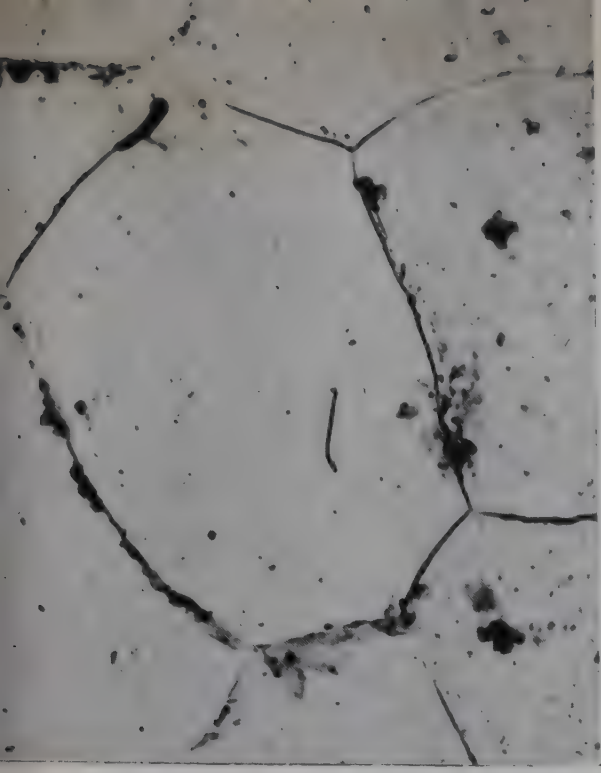
tempering the hardened alloy at 150°C, the lattice parameter value increases to $a = 2.8745$ Å. But tempering at higher temperatures does not change the value appreciably from $a = 2.8745$ Å, though there are very slight shifts towards the value of that of pure iron.

The x-ray diffraction analysis of the extracted carbides from all samples are identified to be $M_{23}C_6$ type where M stands for iron and/or alloying elements. Though there is no change in the nature of carbide by hardening and subsequent tempering, one observation worth mentioning is that there is increased yield of extract with the increase in the tempering temperature.

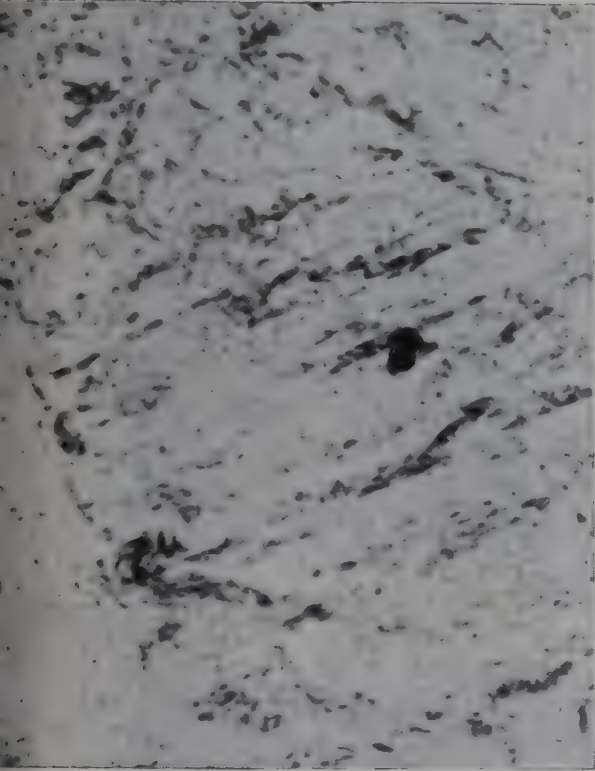
(iii) *Hardness Measurements*: The results of hardness number estimated in Brinell scale are given in Table 1. The hardness number of the hardened alloy was 464 Bhn; tempering at 150°C increased this number to 483 Bhn, but further increase in temperature decreased it. Thus, there was softening upto 350°C, and above 350°C there was practically no change in hardness number upto 550°C but when tempered above 550°C, there was a marked softening and the hardness value came down to that of an ordinary softened steel viz. to 145 Bhn.

Discussion

When steel is quenched from the austenitizing temperature, it produces structures depending upon the rate of cooling. Among these, bainite transformation is regarded as an intermediate reaction between nucleation and growth and martensitic types³⁻⁸. During the austenitizing treatment of a steel, first carbon is redistributed on the solid solution by diffusion and regions of auste-



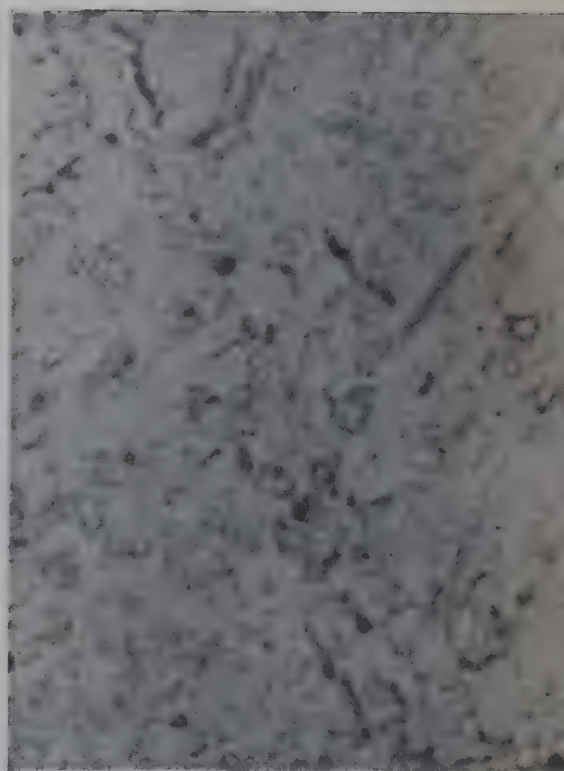
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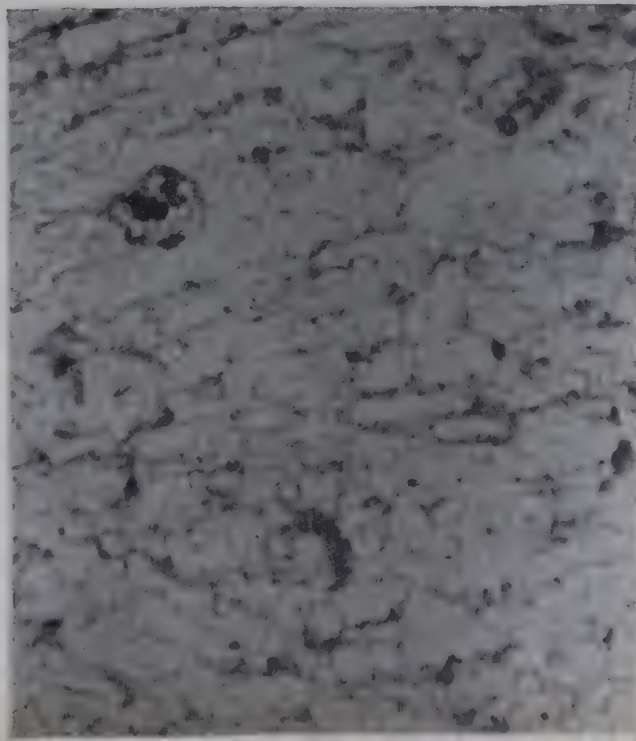
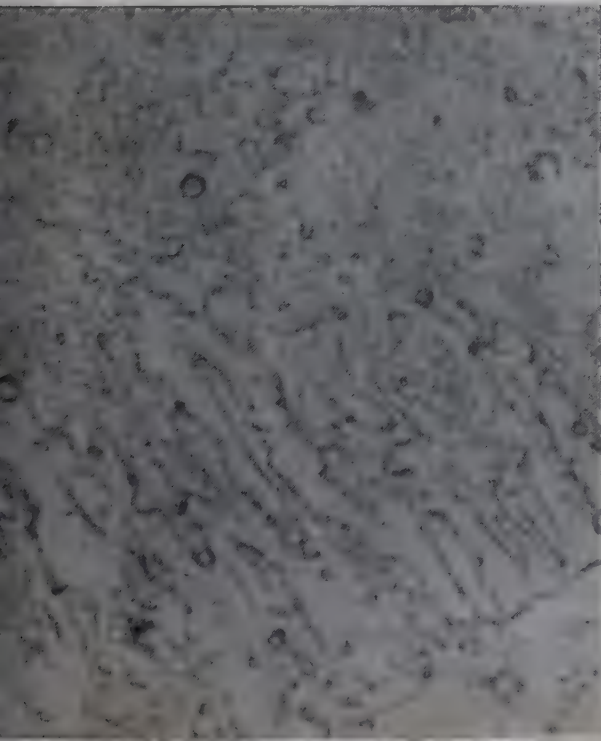
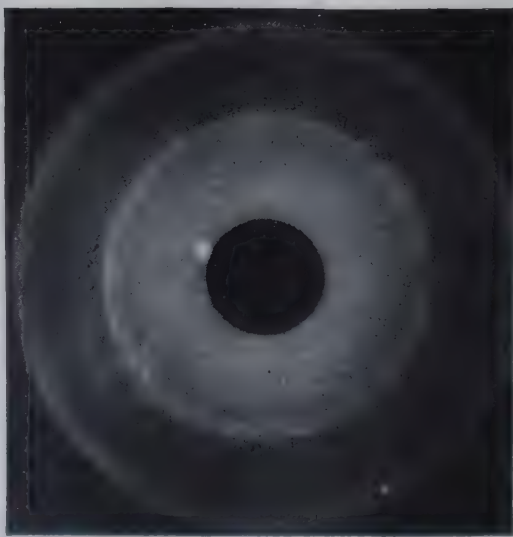


Fig. 1—Electron Micrographs of Low Alloy Steel
 A—Hardened at 900°C ($\times 18000$)
 B—Tempered at 150°C ($\times 18000$)
 C—Tempered at 250°C ($\times 18000$)
 D—Tempered at 350°C ($\times 18000$)
 E—Tempered at 450°C ($\times 18000$)
 F—Tempered at 550°C ($\times 18000$)
 G—Tempered at 650°C ($\times 4000$)



A



B



C



D



E



F



G

Fig. 2—Back Reflection X-ray Diffraction Photographs of Low Alloy Steel (Sharp smaller rings are of α — Fe_2O_3)

- A—Hardened at 900°C
- B—Tempered at 150°C
- C—Tempered at 250°C
- D—Tempered at 350°C
- E—Tempered at 450°C
- F—Tempered at 550°C
- G—Tempered at 650°C

nite, both in rich and poor in carbon in comparison to the initial concentration, is created. This matrix, during cooling undergo a martensitic α transformation. The regions with low carbon concentration undergo diffusionless transformation to a supersaturated solid solution of α phase. The carbon-enriched region of the austenite transforms to a carbon-supersaturated α phase by the martensitic transformation mechanism and the excess carbide is precipitated out. Thus, the bainite transformation by martensitic transformation mechanism bypasses the tetragonal state of martensite to form directly a supersaturated α -phase with precipitated carbides. As martensitic reactions are associated with large stresses⁹, a stable supersaturated α -phase produced by martensitic transformation mechanism could have occurred only if there were microrelief of strain. This would have certainly happened, as was shown by x-ray results of the hardened steel, which indicated a strain-free lattice by the appearance of sharp and resolved 220 reflection of α -structure (Fig. 2A) and very near value of lattice parameter to that of a pure iron. Though the shift in lattice parameter value is inappreciable to indicate any lattice strain, it is appreciable enough to indicate that the ferrite structure with even less than this much difference in lattice parameter can accommodate 0.95 per cent carbon in its interstitial positions to form a carbon supersaturated phase¹⁰. Electron micrograph (Fig. 1A) of the hardened alloy also showed carbide precipitation in a supersaturated ferrite matrix. Moreover, hardness number of this sample showed it to be high (464 Bhn), which is in the range of bainitic structures. Thus, all experimental evidences show that the hardened low alloy steel has taken up a structure nearer to bainite.

Tempering at 150°C results in precipitation of carbide particles (Fig. 1B). This might have happened by diffusionless mechanism, thereby decreasing the carbon concentration in the α -solid solution. This decomposition has grown short and thin carbide plates and the adjacent carbide plates are coherently bonded to the α -solution lattice. Slow nucleation and growth of the carbide plates induce an increase in hardness and a certain amount of elastic stresses in the α -structure lattice as is shown by the diffused and broadened appearance of the 220 reflection (Fig. 2B) and an appreciable increase in the lattice parameter value.

When the tempering is done at 250°C, enlargement of the carbide plates takes place through slow diffusion of carbon within the solid solution. This induces a tendency of coarsening in the precipitation, slightly reducing the hardness value, though without any appreciable change in the lattice parameter value or the amount of elastic

stresses in the α -structure lattice Fig. 2C. The electron micrograph shows (Fig. 1C) that there are growth of carbide plates creating an array of parallel platelets making an angle of about 60° with a common axis. This bainitic structure is similar to the lower bainite or the tempered tetragonal martensite. It may be that the true bainitic structural features have been produced completely only when the hardened steel is tempered at a temperature which is the temperature of isothermal transformation to lower bainite from austenitised steel.

Tempering of the hardened alloy at 350°C appears to have introduced marked changes in the properties of steel. The intense carbide precipitation that has taken place in the form of unresolved stringers without any special orientation to each other and appearance of fine carbides, like in the structure of fine pearlite, shown by electron micrograph resemble to that of upper bainite (Fig. 1D).

This may be due to the reason that tempering of the hardened steel at 350°C has produced features similar to the upper bainite at a temperature around which upper bainite is produced by isothermal transformations from austenite. This microstructural change and the decreased elastic stresses, shown by the decreased broadening of 220 reflection of α -structure in the x-ray photograph (Fig. 2D), would have brought about the appreciable softening in the sample.

The fact that large shift in the hardness number—from 464 to 349 Bhn—has been only due to change in the mode of precipitation of the carbide and not to phase transformation in precipitating carbide has been ascertained by x-ray diffraction analysis of carbides. In fact, a secondary hardening or a retardation in hardening¹¹ should have been observed in this temperature range in an alloy structure due to transformation of epsilon carbide or cementite that were supposed to exist in bainitic and martensitic structures to alloy carbides of lower carbon content. Surprisingly, there were no such carbides nor any transformations and in fact the type of carbide observed throughout were only $M_{23}C_6$. This may be due to the fact that $M_{23}C_6$ type carbide that was existing in the commercial alloy would not have lost its identity, though dissolved in the austenite at the austenitizing temperature because of their isomorphous structures^{12,13}. Therefore, when the steel was hardened to form bainite the carbon-enriched region would have precipitated the excess carbon in the form of $M_{23}C_6$ type by diffusionless precipitation mechanism. Subsequent tempering of this hardened steel at 150° and 250°C also showed the same $M_{23}C_6$ type carbide. This may be due to the reason that in the bainite $M_{23}C_6$ type

carbide already exists and this may induce the same type of carbide formation during further precipitation and growth.

The metallographic structures of the hardened alloy tempered at 450 and 550°C are different from those of the previous ones, because of the higher temperatures the precipitations have been intense and have not formed a particular mode of formation like the previous ones. The final structure is only ferrite and coarse carbides (Figs. 1 E & F). The successive decrease in lattice strain by decreased broadening of 220 reflection (Figs. 2 (E & F)) indicate the accelerated precipitation in these cases. The appearance of globular carbides indicate coagulation and spheroidization by dissolution of smaller carbide particles and growth of larger ones.

When the hardened alloy is tempered at 650°C there are abrupt changes in the properties of steel. There is a complete softening, the hardness number having fallen to 145 Bhn. This may be due to almost total elimination of elastic stresses as shown by the sharp and well-resolved doublet of 220 reflection of α -structure (Fig 2G) and by formation of polygonal ferrite (Fig. 1G). During tempering, there may be coalescence of carbide particles and a grain growth or recrystallization to produce polygonal ferrite grains.

Conclusion

Thus, metallographic, x-ray diffraction and hardness measurement studies reveal that a heat-treated low alloy steel with 0.37 per cent carbon produces supersaturated ferrite phase with fine carbide precipitation, when it is austenitized and then quenched in oil at room temperature. When this hardened steel is tempered at various temperatures, it produces characteristic metallographic structures of lower bainite, upper bainite and ferrite-carbide at temperatures around those of their isothermal transformations from austenitized steel. X-ray diffraction analysis and hardness measurements also confirm the formation of the above phases in the tempered samples.

In all the above transformations, the type of carbide observed is only $M_{23}C_6$ and there is no evidence of epsilon carbide, cementite or any other carbide. Though this observation appears peculiar in bainitic transformations, it may indicate that the kinetics of such transformations are more temperature variant than the type of carbide precipitated¹⁴. It may be that once the supersaturated solid solution of α phase is formed suppressing bainitic transformations, the subsequent transformations become athermal and does not appear to be characterized by the type of the precipitating carbide.

When tempered, the athermal transformations to bainitic structures take place at temperatures related to the activation energy for their growth which may also be the same for their isothermal transformations and the carbide structure may depend upon the retained nuclei of high temperature structure of carbide after quenching. While tempering there is only enlargement of such nuclei. This explains also the reason for non-observance of secondary hardening or retardation in hardening in the above studies, whereas in the case of isothermal transformations there may not be any retained carbide nuclei of high temperature structure and therefore nucleation and growth of different carbides produce the above property changes.

Acknowledgements

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The use of double capillary aspiration system¹ (DCS 1:1), in atomic absorption spectrophotometry, though very useful for routine analysis, reduces the sensitivity to half. This is particularly so when one end of the capillary is employed for continuous aspiration of the releasing agent. To make up the loss of this sensitivity, the above system (1:1) is modified by making the lower arms in the ratio 1:2. To further compensate this loss, use of alcohols with a releasing agent is suggested. Other miscellaneous applications of the system are described.

Applications of Double Capillary in Atomic Absorption Spectrophotometric Analysis

By K. C. SINGHAL, R. C. P. SINHA AND B. K. BANERJEE,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

The dual atomization system used by Alkemade and Voorhuis² and Fukushima³, for investigation of the mechanism of interference, cannot be usefully employed in routine analysis by flame methods. The only advantage of this system over the usual single capillary is slight gain in sensitivity⁴. The Y-shaped double-capillary system (DCS) with equal lower arms (1:1) and its applications in atomic absorption spectrophotometry have been indicated in the earlier paper¹. It has been shown that the titration in true sense can be performed with its help for the elements which are prone to chemical interferences and form nonvolatile compounds in stoichiometric ratio with the interfering ions. The exact end-point can be detected without incurring negative error⁵ as was unavoidable with a single capillary. Its other uses are as follows: standard addition method can be used without adding the standards to the sample, multiple standards can be obtained with the help of a few made ones and interference studies can be performed without tedious sample preparations. The above capillary was found useful and superior to the single capillary in cases where an agent is used for releasing the analyte atoms from interfering ions and where excessive ionization of the analyte atoms is to be inhibited with the help of a salt of an easily ionizable element.

In the double capillary system the sensitivity is reduced to half as the sample is diluted (1:1) during the aspiration process. In the sample solutions where the concentration falls within the optimum working range of the instru-

ment, the decrease in sensitivity is immaterial. When interference of any kind does not occur and calibration method is used, the same sensitivity as that of a single capillary can be achieved by aspirating the sample simultaneously through both the arms. In the cases where one arm is continuously employed for aspirating the releasing agent or salt of easily ionizable elements (to inhibit ionization), the sensitivity becomes half. In the standard addition method also, sensitivity becomes half as the standards and samples are aspirated simultaneously through the separate lower arms. This limitation is significant when the concentration of analyte is near the detection limit.

In view of the above, the existing DCS (1:1) has been modified to DCS (1:2) by varying the lengths of the lower arms. The flow-rate of a solution through an arm is proportional to the length of the other arm. As the flow-rate of the shorter arm of the modified system is higher, the sample is aspirated through it for getting a proportionately high absorption signal. To further compensate for the above loss in sensitivity, the releasing agent (lanthanum chloride) has been mixed with some organic solvent and then used. Other applications of the original as well as of the modified systems have been described.

Experimental

Perkin-Elmer model 303 atomic absorption spectrophotometer and hollow cathode lamps of the same make were used, and the usual single, double¹ (1:1) and

modified double (1:2) capillaries were used for various studies. Analytical conditions were similar to those suggested by Perkin-Elmer⁶.

Modified Double Capillary System: It was made of hypodermic needle no. 22 (Fig. 1), keeping the needle

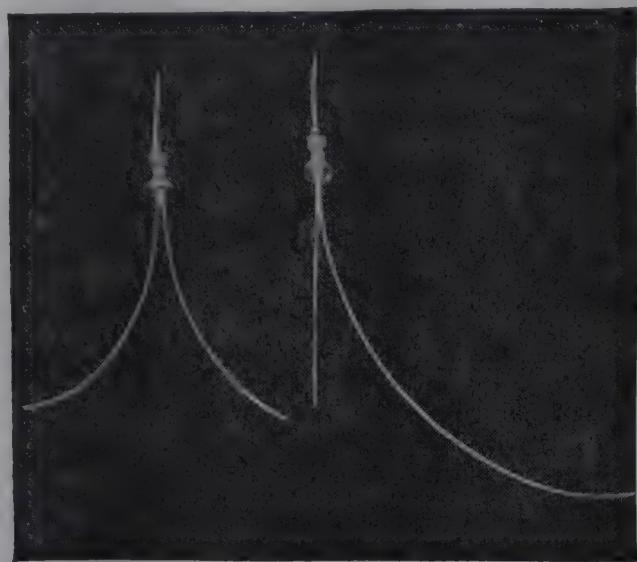


Fig. 1—Original (1:1) and Modified (1:2) Double Capillaries made of Hypodermic Needle No. 22

tube length 0.25 inch. A push-fit socket is made for the base of the needle with two small holes. Two polythene capillary tubes having lengths 3 and 6 inches respectively were inserted through the holes and fixed with an adhesive. The space at the junction of the capillary arms was kept small so that there is negligible time lag between the start of aspiration and the sample reaching the flame. With one inch capillary tube, the needle was connected to the nebulizer. A DCS (1:1) was made as above keeping the length of the two lower arms 3.5 inches. Firstly, a 5 ppm copper solution was aspirated through the longer arm along with water through the shorter one, and then a 2.5 ppm copper solution through the shorter arm and water through the longer one. The length of the arms was adjusted by cutting the ends till the absorptions in both the cases were equal. At this stage the flow-rates of two arms was in the ratio of 1:2. The DCS (1:2), thus made, could also be made by taking two lower capillaries having different inner diam. and adjusting the absorptions as above. In case of DCS (1:2), the sensitivity reduced to 2/3rd when the test element was aspirated through the shorter arm, and to 1/3rd when using the longer arm while with DCS (1:1) it reduced to half. Modified double capillaries with different arm ratios can be similarly made by aspirating standards having concentrations in the same ratios.

APPLICATIONS

Multiple Standards

It has been indicated earlier¹ that a number of standards can be made from a few made ones by using DCS (1:1). It has been found that by using DCS (1:2), even more number of standards are possible from the same set. With two standards, viz. of 2 and 8 ppm, eight standards varying from 1 to 12 ppm can be obtained using the shorter arm as reference. The 2 ppm standard when aspirated through it will give absorption for 2 ppm, whereas when it is aspirated through the longer arm it will correspond to 1 ppm. If both ends are dipped in the above standard, an absorption corresponding to 3 ppm will be obtained. Thus, from only one standard, viz 2 ppm, three standards of 1, 2 and 3 ppm will be obtained. Similarly, 8 ppm solution will give 4, 8 and 12 ppm standards. Now, by aspirating 2 ppm solution through shorter arm and 8 ppm through longer one and *vice versa* two more standards of 6 and 9 ppm respectively will be obtained. Thus, it is seen that by using only two standards of 2 and 8 ppm, eight standards of 1, 2, 3, 4, 6, 8, 9 and 12 ppm respectively are obtained. A calibration curve for copper with above standards is shown in Fig. 2.

Extension of Working Range and Dilution

In atomic absorption spectrophotometry, the optimum working range is very small. The lower range in routine analysis by using a DCS is unchanged as by dipping both the lower arms in the sample an absorbance equal

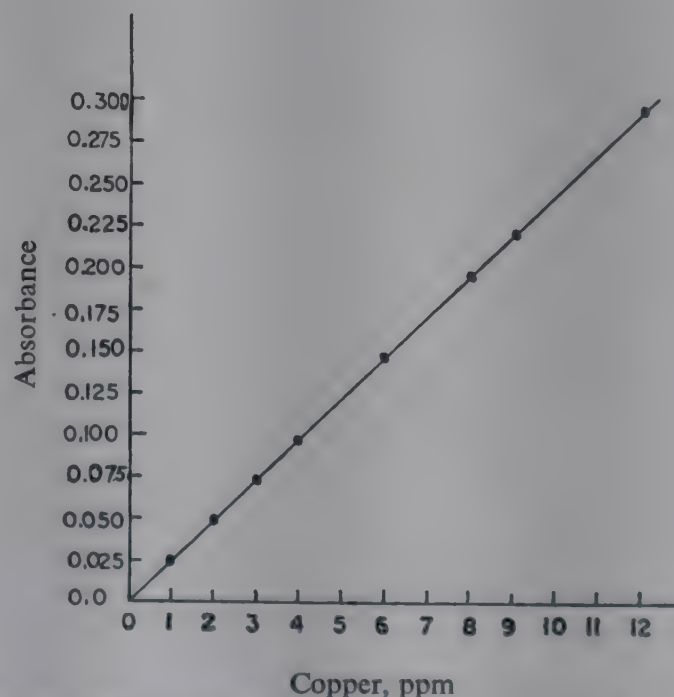


Fig. 2—Calibration Curve for Copper obtained from only Two Standards (2 & 8 ppm) using Shorter Arm of DCS (1:2) as Reference

to that with a single capillary is obtained. The higher limit of the working range is increased 3-fold when the sample is aspirated through the longer arm of DCS (1:2). If the upper working range is 10 ppm, a sample of 30 ppm can be accommodated by aspirating it through the longer arm, without dilution or changing the adjustment of the instrument. This is particularly important when a large number of samples are to be analysed at a time and some astray sample falls outside the higher working range.

Dilution (1:1) has been suggested by Gilbert *et al*⁷ for samples of non-routine nature when interference is suspected. In the presence of interference, corrected value for the diluted sample (1:1), to the first approximation, will be twice the diluted value minus half of the original value obtained. In the analysis of petroleum products⁸, the samples are generally diluted 5 to 10 times with some organic solvent. These dilutions can be achieved by adjusting the arms ratio of a DCS, thereby avoiding a lot of sample preparations.

Standard Addition Method

This method is used for the samples containing high and variable matrix, as it is not always convenient to match the matrix in the synthetic standards. This method of estimation can be simplified by using DCS (1:1) as well as (1:2). The unknown and the standards are aspirated through separate lower arms of the capillary and addition of standards is obtained during the aspiration through the capillary. The effect of matrix in the flame is matched automatically as the sample and standard get mixed at the junction of the capillaries. The effect of urea matrix on the estimation of copper by the addition method was studied. Different copper solutions (1 ppm) containing 1 to 9 per cent urea were prepared and aspirated through the shorter arm of the DCS (1:2) and the standards for addition through the longer one. As the flow rate in the longer arm is half of that in the shorter arm, the addition of the standard will be half of the actual strength. Instead of plotting half of the value, for convenience, the positive side of the abscissa is reduced to half (Fig. 3). It is found that upto 9 per cent urea in the sample, there is no effect on the estimation. This shows that double capillary can be satisfactorily used for routine analysis by above method.

Interference and its Removal

It has been generally claimed that atomic absorption spectrophotometry is free from interferences. In practice, the analysis of a number of elements suffer from chemical interference. Alkaline-earths, in particular, are

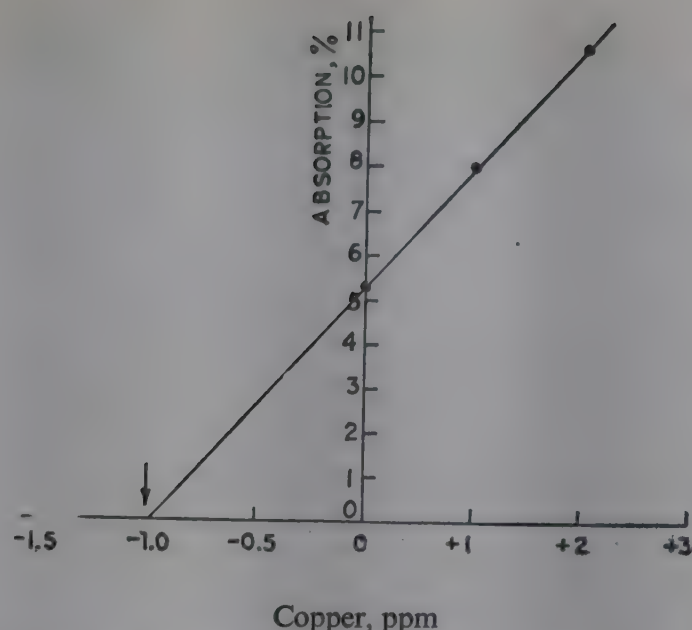


Fig. 3—Standard Addition Curve by DCS (1:2)
(The negative and positive sides of abscissa are plotted in the ratio 2:1)

susceptible to it. The interference takes place only when the test element and interfering ions are intimately mixed. Double-capillary is ideally suited for performing this study. The interference curve can be obtained by aspirating the test element through one arm and the interfering ions through the other. The effect of different alcohols on the interference of phosphorus on calcium is shown in Fig. 4. These studies are done just by making the calcium-phosphorus solutions and aspirating it through one arm and alcohols through the other.

(i) *Releasing Action*: Releasing action is a chemical phenomenon like interference. Since the releasing ion competes with the analyte atom to form the compound with the interfering ions, the releasing will be possible

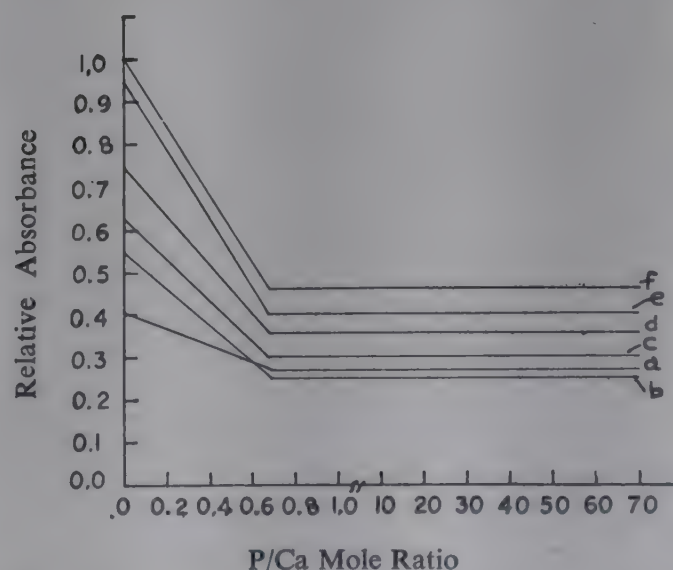


Fig. 4—Effect of Alcohols on 20 ppm Calcium in Presence of Phosphorus

(Alcohols are aspirated through one end of DCS (1:1) and sample through the other: (a) water, (b) methyl alcohol, (c) ethyl alcohol, (d) iso-propyl alcohol, (e) n-butyl alcohol, (f) iso-amyl alcohol.)

only if they are mixed together. The DCS is a convenient means to carry out the automatic mixing during aspiration. In usual analysis of alkaline-earths, 1 per cent lanthanum (as chloride) is used in the solution. For one unknown sample, generally 25 ml. solution is prepared which contains 0.25 g. of lanthanum. Out of this, only about 0.5 ml. is aspirated for analysis (i.e. about 0.005 g. lanthanum is consumed) and rest of the solution goes waste. Similar wastages will be there for standard solutions also. By using the DCS (1:1), 25 ml. of 2 per cent lanthanum solution can be used for the analysis of about 100 samples. This is a great saving in the consumption of the reagent and a lot of time and botheration for sample preparation is also saved.

As mentioned earlier, the practical limitation of DCS (1:1) for the releasing purpose is the reduction of the sensitivity to half. Use of DCS (1:2) partly compensates for this. The sample is aspirated through the shorter arm and a 3 per cent lanthanum (as chloride) solution through the longer one. In this way 2/3rd of the original sensitivity is obtained. The releasing action of lanthanum chloride in aqueous solution is shown in Fig. 5a. For this purpose, the capillary ratio is not very critical as it may vary only slightly the flow-rate of the sample which is immaterial.

Lanthanum nitrate was used by Tenny⁹ for releasing calcium from ions, like phosphorus etc. In the course of releasing studies it was observed that if lanthanum as nitrate (instead of chloride) is used, it depresses the calcium and strontium signals and does not remove the phosphorus and aluminium interferences. It has been also observed that if a 2 per cent lanthanum as

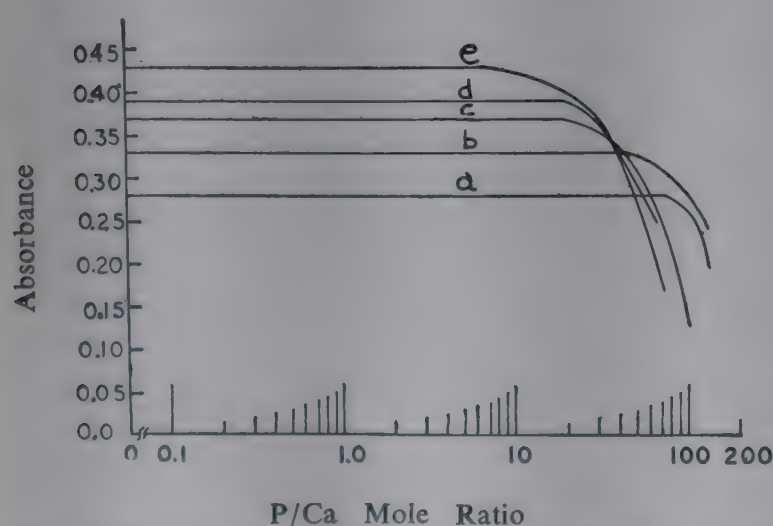


Fig. 5—Release of 10 ppm Calcium from Phosphorus by Lanthanum as Chloride Mixed with Different Alcohols Aspirated Through the Longer Arm of DCS 1:2

- a—3% lanthanum—water
- b—3% lanthanum—8% n-butyl alcohol
- c—3% lanthanum—50% methyl alcohol
- d—3% lanthanum—50% methyl alcohol
- e—3% lanthanum—50% iso-propanol

nitrate solution having 2 per cent hydrochloric acid is used, it enhances the absorption of calcium and strontium by about 30 per cent. This indicates that for removal of interference, the presence of chloride ion along with lanthanum ion is necessary.

(ii) *Use of Organic Solvents*: Properties, like vapour pressure and vaporization rate, which are higher for alcoholic solution than for the aqueous one, and surface tension, which is lower (resulting in the formation of smaller drop size), contribute to the enhancement of the absorption signal. These properties are also supposed to minimize the chemical interference. Gibson *et al*¹⁰ have shown that the small drop-size may completely eliminate the interference. Smith and Winefordner¹¹ did not observe the phosphorus interference in very dilute calcium solution in premix laminar flame. Lockyer *et al*¹² have studied the effect of organic solvents and found that 50 per cent isopropanol increases the sensitivity by 2 to 10 times. As the reduction factor for sensitivity in case of DCS is only 2 or less, it is possible to use organic solvents with it to achieve a higher sensitivity. The effect of alcohols on the calcium-phosphorus system is studied by passing 20 ppm calcium solution with increasing phosphorus concentrations through one arm of DCS (1:1) and alcohols, as such, through the other. It is observed (Fig. 4) that with higher carbon atoms of the alcohol the calcium absorption increases. When n-butanol (8 per cent miscible) is aspirated, the enhancement is 140 per cent and when *iso*-amyl alcohol (immiscible) is used the enhancement is about 150 per cent. The flow rate of the organic solvents was not taken into account. It is also observed that the degree of interference due to phosphorus in alcoholic solution is more than that in the aqueous one. When P: Ca mole ratio is more than 2:3 in neutral flame, it is 52 to 58 per cent for alcoholic solution and 33 per cent for aqueous one.

These solvents can be used with the releasing agent to further compensate the loss in sensitivity due to use of the DCS. In Fig. 5, the release of 10 ppm calcium from phosphorus by 3 per cent lanthanum (as chloride) solution mixed with different alcohols using DCS (1:2) is shown. The releasing agent mixed with alcohols was aspirated through the longer arm and 10 ppm calcium solution, containing increasing amount of phosphorus, through the shorter one. It has been found that when DCS (1:2) is used for releasing purpose with the agent mixed with alcohol, it gives about 25 per cent higher absorption than that obtained for aqueous solution with a single capillary. The alcohols are preferred because they give smooth burning of the flame and en-

hance the signal considerably. It has been found that 8 per cent *n*-butanol, when mixed with 3 per cent lanthanum (as chloride), protects the calcium from about 70 mole excess of phosphorus. When methyl and ethyl alcohols are used, only 20 mole excess of phosphorus can be tolerated and in case of *iso*-propanol the tolerance is even less. The use of *n*-butanol is suggested along with the releasing agent as the limit of tolerance is as high as that with the lanthanum aqueous solution. Its use will be economical, as only 8 per cent (partly miscible) is required when using DCS (1:2).

The observed increase in the degree of interference due to phosphorus and lowering of the tolerance limit in presence of alcohol is not in agreement with the explanation based on the properties mentioned above and it is difficult to explain.

(iii) *Effect of Burner Height*: The degree of interference due to the ions, like phosphate and sulphate, on alkaline-earths decreases with the burner height^{11,13}. This is due to gradual decomposition of their involatile compounds during their transit in the flame. Fassel and Becker¹³ have recently observed that the phosphate interference on alkaline-earth completely disappears at a height of 20 mm above the base of the flame. The studies at different burner heights using the DCS (1:1) was made. It is clear from Fig. 6 that in presence of ethyl alcohol more than 130 mole excess of phosphorus can be tolerated at 33 mm. observation height of the flame, though the sensitivity decreases considerably. When *iso*-amyl alcohol (immiscible) is aspirated in a reducing flame more than 130 mole excess of phosphorus can be tolerated and the sensitivity is about 2/3rd of that of aqueous solution when aspirated through a single capillary.

Miscellaneous Applications

(i) *Use for the Study of Immiscible Solvents*: An interesting point, observed during the experiments, was

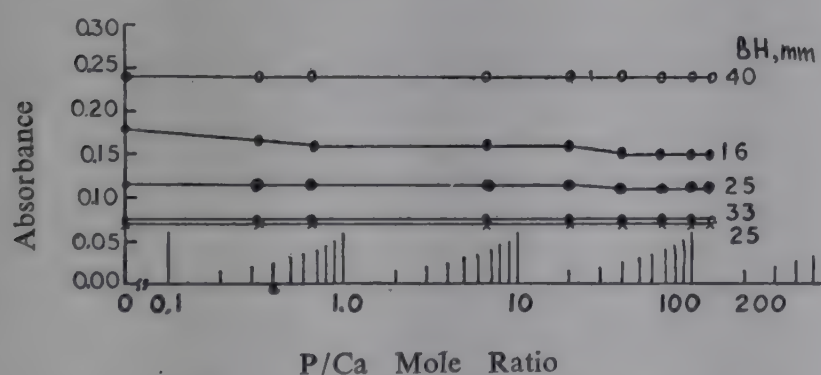


Fig. 6—Effect of Burner Height on the Interference due to Phosphorus on Calcium (10 ppm) in Presence of Alcohols Aspirated through one Arm of DCS 1:1

x - x Water
 ●● Ethyl Alcohol
 o-o Iso-amyl Alcohol

that the effect of immiscible and partly miscible organic solvents on the aqueous solution of a test element can be studied very conveniently with the help of a DCS. Enhancement in the calcium signal due to *n*-butanol (8 per cent soluble) and *iso*-amyl alcohol (immiscible) aspirated through one arm was observed [Figs. 4 (e & f)] without extracting it in them and no fluctuation in the readings was found. It appears that when the aqueous solution of test element and the immiscible organic solvent are mixed at the junction of the DCS, the physical properties of this suspension affect the atomization of the test element.

(ii) *Use in Internal Standardization*: The DCS arms can be employed for aspirating the sample and the internal standard. In flame emission spectrophotometry the internal standardization is quite common. Recently, Feldman *et al*¹⁴ have estimated major elements in stainless steel using internal standardization technique, which gives more accurate results.

Conclusion

The double-capillary system (DCS) can be widely used for routine analysis by flame techniques. Its limitation due to the loss of sensitivity can be overcome, partly by varying the lengths of the arms and rest by use of organic solvents. By using a releasing agent with alcohol, a 25 per cent gain in sensitivity over that of aqueous solution by single capillary was obtained. In the case of the standard addition method, it has been found that high solid content behaviour with DCS is similar to that with single capillary. It is suggested that the DCS can be used for a number of miscellaneous uses, e.g. in the preparation of multiple standards, for increasing the working range, for dilution of the samples, for the study of immiscible solvents and for use in internal standardization. This capillary system has been found very useful, particularly, when a large number of samples are to be analysed. Its use saves a lot of sample preparation time and economizes the use of the reagents. The DCS (1:2) can also be used for titration and inhibiting ionization in a way similar to DCS (1:1), which has been discussed earlier¹.

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Suggestions have been made for utilizing manganese concentration in calcium carbonate minerals as a significant guide for manganese ore prospecting, and also as an index for establishing relative ages of samples belonging to unclassified periods. ESR spectrometry provides a very sensitive and elegant tool.

Geological Applications of ESR Spectrometry : Mn²⁺ Ions in Calcium Carbonate Minerals

By P. K. GHOSH, M. SAMADDAR, S. C. SINHA,
J. S. TIWARI AND A. C. BANERJI,

*Planning & Development Division,
The Fertilizer Corporation of India Ltd., Sindri, Bihar*

Calcium carbonate minerals commonly used in the fertilizer industry, viz. calcite, limestone and dolomite of non-biological origin, have an affinity for Mn²⁺ ions. Indeed a continuous isomorphous series may form starting with calcite (CaCO₃) and ending with rhodochrosite^{1,2} (MnCO₃). The physical aspects of Mn²⁺ ESR spectrum in calcite have been discussed by Lazukin and Terentevsky³, who had interpreted the hyperfine structure of the spectrum in terms of the transitions $\Delta m_I = 0, \pm 1$ and ± 2 , the last two being forbidden transitions. The aim of the present work is to show how a study of ESR spectra of these minerals can be applied to elicit geological informations regarding them in a simple manner.

Experimental

Different calcium carbonate minerals collected from

widely differing localities were studied. The samples, corresponding localities and their disposition with respect to the manganese bearing zones are indicated in Fig. 1.

Equal weighed amounts (100 mg. approx.) of the powdered samples were taken in thin walled silica tubes and studied at room temperature in an X-band ESR spectrometer fitted with a TE₁₀₂ mode rectangular cavity. The amplifier gain was kept at a fixed value throughout the experiment. The large changes in the signal strength due to different concentrations of Mn²⁺ ions encountered in the samples were compensated by adjusting the 100 kHz modulation voltage, taking advantage of the fact that the amplitude of the recorded signal (derivative of the absorption signal) is proportional to the modulation amplitude. Independent measurements of the manganese concentrations were carried out by optical spectrometry and polarography and further

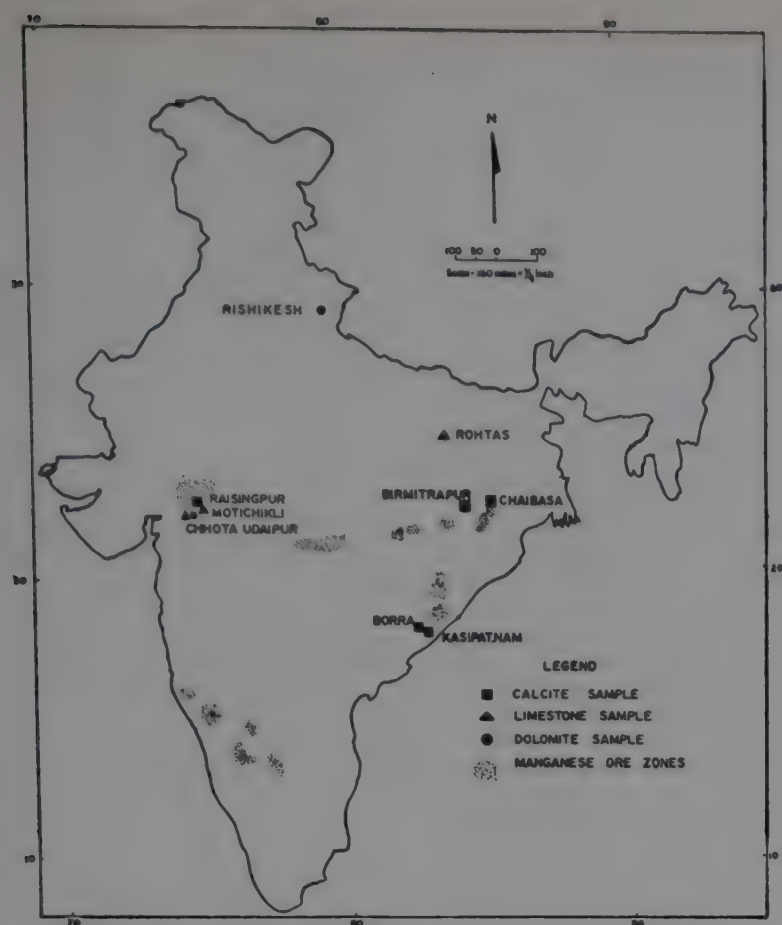


Fig. 1—Map of India showing Sampling points

confirmed by atomic absorption spectrophotometry to show that the findings of the ESR experiments are reliable enough.

Results

The ESR spectra are reproduced in Fig. 2. The ordinate scales are different for the different spectra as indicated by the multiplying factors given alongside, x2 for example, means that the ordinate scale has been expanded by a factor 2. The mean g-value is 2.004, with an isotropic hyperfine splitting const. $A=93.7$ Oersteds approximately.

The manganese concentrations in the samples, as determined spectroscopically, are shown in Table 1 below.

TABLE 1—CONCENTRATION OF MANGANESE DETERMINED BY SPECTROSCOPY

Sl. No.	Description of Sample and Place of Collection	Manganese Concentration, % (Approx.)
1.	Blue Calcite (Borra)	0.001
2.	Light Yellow Calcite (Borra)	0.001
3.	Pink Calcite (Kashipatnam)	0.1
4.	Light Green Calcite (Chaibasa)	0.1
5.	White Calcite (Birmitrapur)	0.4
6.	Calcite (Raisinghpur)	0.16
7.	Limestone (Motichikli)	0.05
8.	Limestone (Chhota-Udaipur)	0.005
9.	Dolomite (Chhota-Udaipur)	0.05
10.	Limestone (Rohtas)	0.0001

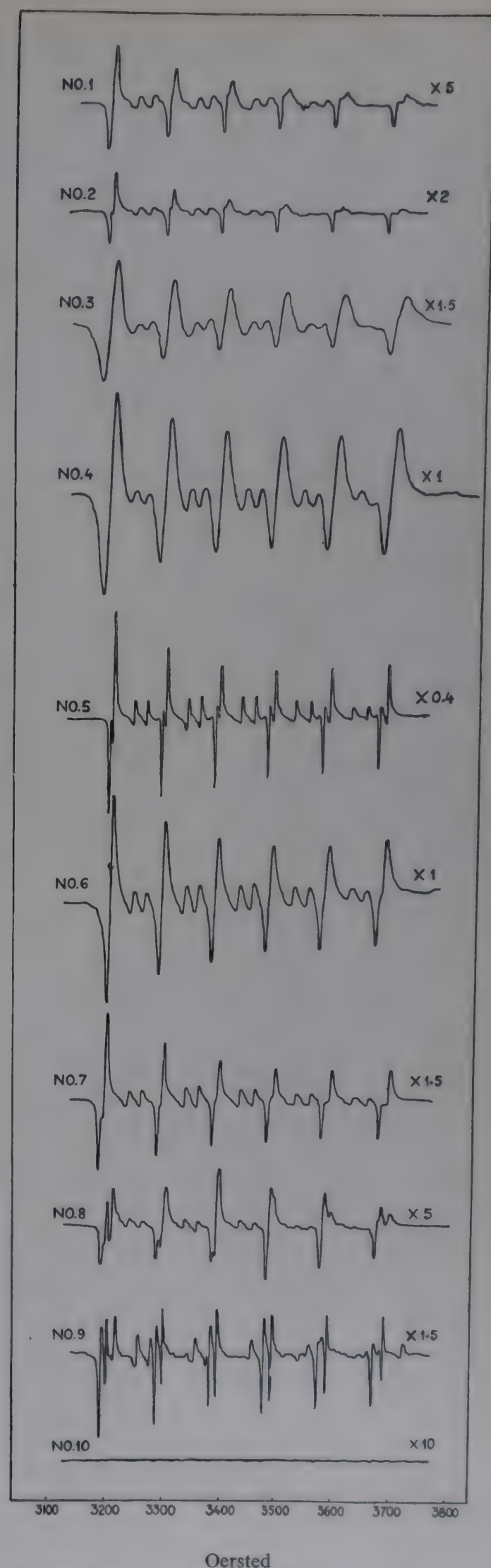


Fig. 2—ESR Spectra of Different Calcium Carbonate Samples

Discussions

The g -value and the well-resolved hyperfine structure of the ESR spectra are typical of Mn^{2+} ions dispersed in the lattice, which shows that manganese is incorporated in the minerals themselves, and does not exist as an isolated phase.

The origin of all calcium carbonate minerals can be traced back to aquatic sources—whether marine or fresh water—and manganese, if present in that source, would be incorporated in the mineral lattice. Evidence exists that bivalent manganese ions from minerals can go into solution in aqueous media much more readily than the ions in the higher valency states⁴, and it is understandable that the manganese ions incorporated in the lattice of the calcium carbonate minerals should always be in the bivalent state. Now, for fresh water sources formed by accumulation of rain-water draining the surface layer of earth's crust, an appreciable concentration of Mn^{2+} ions can build up only if suitable manganese ore bodies were present nearby within approach of the water. Similar arguments hold for subterranean water also. For marine deposits, however, such a strictly local effect can never be expected.

A scrutiny of Table 1 together with Fig. 1 immediately shows that the samples collected from within the manganese-bearing zones are considerably richer in Mn^{2+} ions than those collected outside such zones. A ready field of application suggests itself, viz. prospecting for manganese. The calcium carbonate minerals are very widely distributed in nature and measuring the Mn^{2+} ion content in these can provide a valuable clue for locating manganese ores.

Another significant aspect may also be derived from an extension of the above argument. It may be observed that even within the manganese-bearing zones, the signal intensity, i.e. the manganese concentration, varies widely even though the nature of the minerals concerned remains the same. In some cases, the Mn^{2+} concentrations are too low to be explained by temperature effects or change in solubility due to interference by other ions. Applying the argument mentioned before, it can be stated that the samples showing such significantly low concentration of Mn^{2+} (as with the samples from Borra), even though lying in the manganese-bearing zones, must have been formed at a time when such large amounts of manganese ores were not present. Carbonate beds appearing in later horizons always show large concentrations of Mn^{2+} . (One has to consider the possibility of diffusion of manganese into previously formed calcium carbonate beds also. But such cases should be identifiable by a Mn^{2+} concentration gradient

which should be always an observable characteristic of the downward diffusion. Proper sampling at different thicknesses can detect the gradient, if it exists, and thus remove the ambiguity.) Therefore, if it is found that a calcite sample from a manganese ore belt contains very little Mn^{2+} ions, then the calcite must antedate the adjacent manganese ore. Conversely, a high Mn^{2+} concentration in bulk will indicate comparatively later age of formation. Thus, a means for establishing the paragenetic sequence, primitive carbonates—manganese ore—later carbonates is envisaged. Knowing the age of one in this sequence can serve to identify the relative ages of the other two. A table is now drawn, incorporating the present knowledge about the geological ages of the samples studied and their adjacent manganese ores (Table 2).

Let us consider the example of the samples from Andhra Pradesh. The manganese ore body in this region is derived from Kodurite of an uncertain age. The associated rock of the crystalline calcite samples from the Borra cave are Khondalites and Charnockites, whose age, from K^{40}/Ar^{40} ratio determinations⁶, appears to be 450-510 million years, and from whole rock Sr-Rb isochron determinations⁷ 1300-1520 million years while the Pb-isotopic age⁸ is *c.* 2600 million years. However, the Kodurite rocks appear to be younger than the Charnockite-Khondalites, as its origin is assumed to be due to intrusion of granite into the Khondalites⁹. As may be expected, the samples from Borra cave contain very little manganese. Calcites from the nearby Kashipatnam area show a much larger manganese concentration, indicating a later age of formation. It is apparent that three major metamorphic-plutonic cycles closing at *c.* 2600, *c.* 1500 and *c.* 500 million years are recognisable in this region. From all the available evidences, the Borra cave calcite appears to be related to the *c.* 1500 million years event.

A similar correlation may be observed in the samples collected from Gujarat area. The archaean limestone from Chhota-Udaipur (sample No. 8) shows a significantly lower Mn^{2+} concentration as compared to the cretaceous¹⁰ calcite (sample No. 6) and limestone (sample No. 7) from the Bagh bed at Raisinghpur and Motichikli. The adjacent manganese ore body is derived from Gondite which is correlated to the precambrian Sausar group¹¹, metamorphism and granitisation of which closed at 864-996 million years based on K-Ar ages¹². The dolomite sample (No. 9) from apparently the same horizon as the Chhota-Udaipur limestones however shows an appreciable signal, a fact rather difficult to explain. But the local geology points to the possibility

TABLE 2—GEOLOGICAL AGES OF MANGANESE ORES STUDIED

Sl. No.	Description of Sample	Place of Collection	Relative ESR-Signal Strength	Adjacent Mn Ore or its Parent Body	Geological Age of Mn Ore	Age of Sample	Remarks
1.	Blue Calcite	Borra Cave (Andhra Pradesh)	0.094	Kodurite ⁵	1500 million years ⁹	1500 m.y. ⁷	Associated rocks of Borra calcites are Khondalites and Charnockites
2.	Light yellow calcite	"	0.16	"	"	"	"
3.	Pink calcite	Kasipatnam (Andhra Pradesh)	8	"	"	510 m.y.(?) ⁸	Associated with Granulites, which are the parent bodies
4.	Light green calcite	Chaibasa (Bihar)	9.5	Residual concentration ¹²	—	2700 m.y	
5.	White calcite	Birmitrapur (Orissa)	24	"	—	840-990 m.y. ¹⁶	Derived from Gangpur Sediment
6.	Calcite	Raisinghpur (Gujarat)	10	Gondite	864-984 m.y. ¹¹	140 m.y. ¹⁰	Cretaceous ¹⁰
7.	Limestone	Motichikli (Gujarat)	5.1	"	"	"	"
8.	Limestone	Chhota-Udaipur (Gujarat)	1.2	"	"	Archaean	
9.	Dolomite	"	5.9	"	"	"	
10.	Limestone	Rohtas (Bihar)	Just detectable	—	—	600 m.y. ¹¹	Lower Vindhyan

that the dolomites were formed from the limestones by the action of magnesium-rich solutions, which had resulted in the replacement of calcium by magnesium. The dolomites thus may be actually younger than the limestones.

A comparable example from the Bihar-Orissa belt is found in the Chaibasa and Birmitrapur calcite samples. The fine-grained calcite (sample No. 4) from Chaibasa is intrusive into the Iron Ore group rocks, metamorphism of which closed at 2700 million years¹³. The adjacent manganese ore body was formed by residual concentration¹⁴, of the previously existing Gondite. This explains the large manganese concentration in the Chaibasa calcite. The large white crystals of calcite (sample No. 5) collected from Birmitrapur area had apparently formed by later recrystallization due to hydrothermal processes from the limestone deposits of the original Gangpur sediments, metamorphism of which closed at 846-950 million years¹⁵. The resultant solubilization of the Mn²⁺ ions from the manganese ore body already present then can adequately explain the very large amplitude of the ESR signal in this sample, much larger indeed than that for sample No. 4.

The Vindhyan limestone (sample No. 10), from Rohtas, away from the manganese belts, shows a very poor Mn²⁺ concentration, as may be expected.

Some limestones and dolomites of marine origin and of comparatively recent date from the Himalayan region were also studied. They all gave fairly strong Mn²⁺ ESR signals. The doubling of lines observed in many of the samples arises from the fact that partial replacement of calcium by magnesium results in the formation of two inequivalent sites. Thus, the effect is strongest in dolomite.

Conclusions

The problem of age determination of geological specimens belonging to the archaean-precambrian period remains very difficult owing to the absence of fossil remains and suitable radio-elements in the rocks. Recent mass-spectrometric determinations of K: Ar, U: Pb, Th:Pb and Rb:Sr ratios have made it possible to determine the age of such samples in some cases. The premises presented here may provide further means for relative age determinations in a limited way. The principle can possibly be extended to cover other ore body-

sediment systems, both from the point of view of prospecting and age determination. The use of ESR in these applications, when permissible, has the advantages of high sensitivity, simplicity of operation and elimination of time-consuming sample preparation techniques required in other methods. The product of ESR line width into the signal height itself can be accepted as a measure of relative concentration. It should be emphasized that the paper, in its present form, tries to put forward a principle rather than experimental data. More extensive data on a much larger number of samples are being collected and will be published later.

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Thermogravimetric and differential thermal analyses of some urea complex compounds formed by interaction of urea with nitric and phosphoric acids, ammonium and calcium salts have been made with particular reference to their stability below 100°C and decomposition characteristics at high temperatures. It has been observed that the nitrate and phosphate of urea as well as its complexes with ammonium chloride/nitrate and calcium nitrate decompose to a small extent in the temperature range 60-100°C liberating ammonia. There is, however, no such decomposition of those mechanical mixtures of urea with similar constituents where complexes are not formed. Of these complexes, urea-ammonium nitrate and urea-ammonium chloride, formed by recrystallizing from the solution (1:1 molar ratio), are very unstable and they dissociate into the individual components below 80°C. Again, unlike urea, its complexes with nitric acid as well as ammonium salts decompose completely into gaseous products by 350°C, whereas those with phosphoric acid and calcium nitrate do not do so even when heated upto 850°C. Furthermore, with dicalcium hydrogen phosphate urea does not form any complex but there is interaction of the individual components during decomposition at high temperatures.

Thermal Studies on Some Urea Complexes Of Compound Fertilizers

By H. ROY AND H. ACHARYYA,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

Urea is used as one of the constituents in the nitrogenous fertilizer formulations. It is known that it forms adducts with many of the phosphatic and nitrogenous compounds¹. With monocalcium phosphate, it forms the adduct, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$, which is stable and non-hygroscopic². But as a result of the formation of this adduct, the water of crystallization is released from monocalcium phosphate monohydrate. This free water forms a saturated solution which generates enough liquid to cause stickiness and caking of compound fertilizer containing urea and superphosphate. The adduct, $\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_4\text{Cl}$, formed by urea with ammonium chloride is reported to be responsible for the enhanced caking property of the compound fertilizers containing urea and potassium chloride³. With calcium nitrate, the complex compound $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ is formed^{4a}; this compound is less hygroscopic than calcium nitrate. With ammonium nitrate two uncongruently melting binary compounds are formed⁵, viz. $\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_4\text{NO}_3$ and $\text{CO}(\text{NH}_2)_2 \cdot 2\text{NH}_4\text{NO}_3$. But it has been observed that mixtures of fertilizers containing urea and ammonium nitrate are very hygroscopic¹. Other compounds of urea, like phosphate ($\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$) and nitrate ($\text{CO}(\text{NH}_2)_2 \cdot$

HNO_3), are also known^{6,7}. Very little is known on the thermal stability and high temperature changes of these urea complex compounds, although those of complex-forming individual constituents as well as their compound fertilizers have been reported⁸⁻¹⁰. The physical characteristics, such as caking, nitrogen loss, etc., of the compound fertilizers containing these complexes, are very much influenced by their thermal stability. To understand the mechanism which leads to such physical characteristics, precise knowledge of the thermal changes and decomposition characteristics of the urea-complex compounds is necessary. Such a study is expected to throw much light on minimizing the cost of storing, bagging, handling, transporting and applying farm fertilizers.

Experimental

Urea complex compounds were prepared from A. R. grade reagents. The procedure for preparation is outlined below:

(i) *Urea Nitrate*: The procedure followed for preparing this compound is almost similar to that reported by Vogel⁷. In a saturated solution of urea, nitric acid (conc.) was added dropwise as a result of which a white, finely divided precipitate of urea nitrate separated from

the solution. The resulting mass was filtered and washed with a very small amount of ice cold water, and then pressed and dried in air.

(ii) *Urea-Ammonium Nitrate*: 50 cc of 1 molar solution each of urea and ammonium nitrate was mixed thoroughly and evaporated to almost dryness over a hot plate at 50°C. The solid product, thus obtained, was amorphous and found to be very hygroscopic.

(iii) *Urea-Calcium Nitrate*: The procedure followed is the same as reported by Waesser¹¹. 3g. each of urea and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (1:4 molar ratio) was dissolved in 50 cc. of distilled water and evaporated to dryness over a hot plate at 50°C.

(iv) *Urea-ammonium Chloride*: The procedure followed was same as reported by Lehr *et al*⁴. In this method solid ammonium chloride was added to a saturated solution of urea at 50°C and cooled to the room temperature (27°C), when a crystalline solid product separates out.

(v) *Urea Phosphate*: The procedure followed is the same as reported by Waggaman⁶. Urea phosphate was obtained by dissolving urea in 85 per cent phosphoric acid and heating over a hot plate to 50°C for $\frac{1}{2}$ hr. The solution was stirred vigorously from time to time and the crystals separated out on cooling.

(vi) *Urea-Dicalcium Hydrogen Phosphate*: 3 g. of urea and 1.3 g. of dicalcium hydrogen phosphate were mixed in 50 cc distilled water. The suspension was slowly evaporated to dryness over a hot plate at 50°C.

(vii) Synthetic mixtures of urea with each of (a) ammonium nitrate, (b) calcium nitrate tetrahydrate, (c) ammonium chloride and (d) dicalcium hydrogen phosphate respectively were prepared by mixing the components in an agate mortar in the same proportion as used for recrystallizing from solution in a humidity-controlled room (at 27°C and 60 per cent relative humidity).

The recrystallized and mechanically mixed products were kept in a desiccator over anhydrous silica gel for 24 hr.

Thermogravimetric Analysis: Thermogravimetric analysis of these samples as well as some individual constituents was performed in an apparatus fabricated in this laboratory¹². For samples without phosphatic compounds and calcium nitrate, the maximum temperature attained was 450°C, and for the rest upto 850°C. The rate of rise of temperature was maintained at 10°C/min. The decomposition data at different temperatures are given in Table 1. The derivative thermogravimetric analysis (DTGA) curves obtained from TGA data

($\frac{dw}{dt}$ vs $t^\circ\text{C}$) of these samples are shown in Figs 1 (A & B).

TABLE 1—WEIGHT-LOSS OF UREA COMPLEXES AND THEIR CONSTITUENTS AND MECHANICAL MIXTURES

Sample	Weight-Loss at Different Temperatures %			
	80°C	350°C	450°C	850°C
1. Urea	0.09	84	99	—
2. Urea-Nitrate	0.69	100	—	—
3. Urea-Ammonium Nitrate	2.90	99	—	—
4. Urea + Ammonium Nitrate	0.02	100	—	—
5. Urea-Calcium Nitrate	1.50	60	75	87
6. Urea + Calcium Nitrate	0.72	59	68	87
7. Urea-Ammonium Chloride	0.52	99	—	—
8. Urea + Ammonium Chloride	0.05	96	—	—
9. Urea-Phosphate	1.8	23	27	98
10. Urea-Dicalcium Phosphate	0.16	45	52	53
11. Urea + Dicalcium Phosphate	0.12	45	52	55

Differential Thermal Analysis (DTA): The differential thermal analysis of these samples was performed in a manually operated apparatus fabricated in this laboratory¹². The temperature range was 27 to 450°C for urea-ammonium nitrate/chloride and upto 850°C for urea-calcium nitrate and urea-phosphate systems. The sample-holder was made of thin platinum sheet in the form of a cylinder. The thermocouple used for this purpose was chromel/alumel. The rate of rise of temperature was maintained at about 3°C/min. upto 100°C and 10°C/min. afterwards. The temperature of the furnace was recorded by a suitable temperature-indicator having an accuracy of $\pm 2.5^\circ\text{C}$. The reference substance used was ignited alumina. The DTA thermograms are shown in Figs 2(A & B).

Results and Discussion

The decomposition characteristics of urea at high temperatures are known^{4,13}. Urea melts at 133°C and then decomposes at higher temperature to ammonia, carbon dioxide and cyanic acid. At 150-160°C it decomposes to yield ammonia, ammonium cyanate and biuret. As the temperature is raised, cyanic acid is formed from these decomposition products. This acid is volatile but it polymerizes easily to form cyanuric acid and ammelide. These sequences are also evident in the DTGA thermogram of urea, which shows three decomposition steps at 140-260°, 320-380° and 380-440°C

Fig. 1 (A & B)—DTGA Thermograms of Urea Complexes, Their Constituents and Mechanical Mixtures

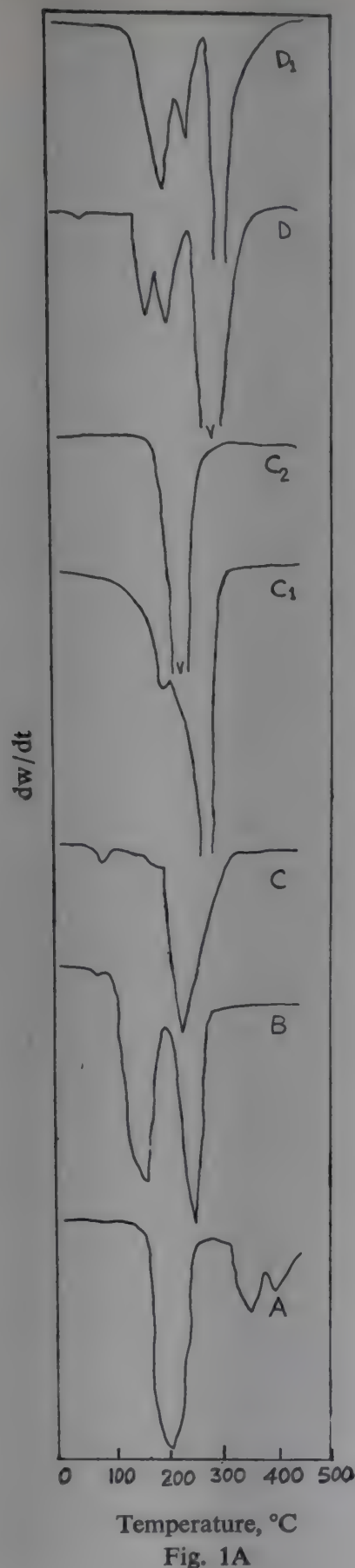
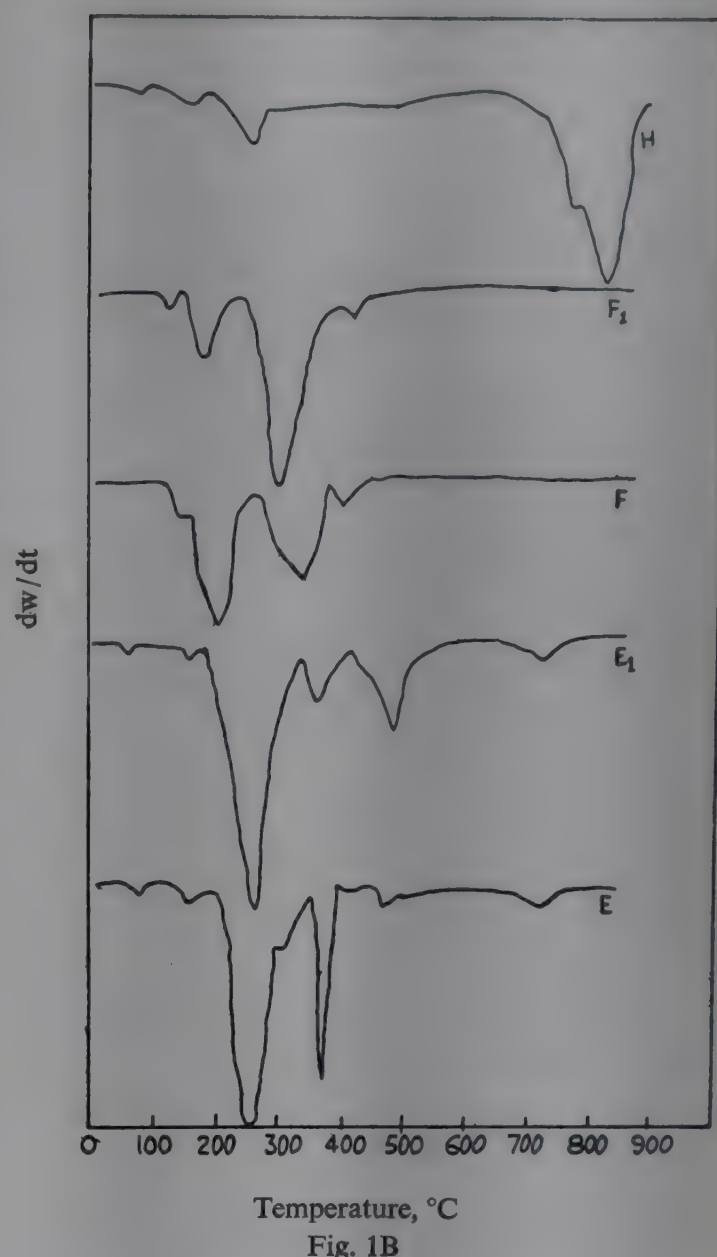


Fig. 1A—A —Urea
B —Urea-Nitrate
C —Urea-Ammonium Nitrate
G₁—Urea + Ammonium Nitrate
C₂—Ammonium Nitrate
D —Urea-Ammonium Chloride
D₁—Urea + Ammonium Chloride

Fig. 1B—E —Urea-Calcium Nitrate
E₁—Urea + Calcium Nitrate
E₁—Urea + Calcium Nitrate Tetrahydrate
F —Urea-Dicalcium Hydrogen Phosphate
F₁—Urea + Dicalcium Hydrogen Phosphate
H —Urea-Phosphate



compound. The thermograms (both DTGA & DTA) of urea complexes and the synthetic mixtures differ from those of urea. The essential features of this difference are discussed below.

Urea Nitrate and Urea-Ammonium/Calcium Nitrate System: From the DTGA thermogram of urea nitrate, it is evident that it decomposes in three steps, viz. at 70-100, 100-200 and 200-280°C (Fig. 1A). Of these steps, the first one is very weak indicating decomposition occurring to a very small extent. In fact this decomposition is not indicated in the DTA thermogram (Fig. 1A) which shows only two endothermic peaks at 120 and 220°C corresponding to the last two decomposition steps. When this compound is kept at 70°C for 15 min., there is a weak smell of ammonia. Again, the complex loses 100 per cent weight at 350°C whereas there is only 84 per cent weight-loss in case of urea (Table 1).

The DTGA thermogram of urea-ammonium nitrate recrystallized product is similar to that of their mechani-

(Fig. 1A). The first step is due to the decomposition of urea to ammonia, ammonium cyanate and biuret and the later steps which are weak in comparison to the former one due to formation and volatilization of cyanic acid. There is, however, one strong endothermic peak at 140°C in the DTA thermogram of urea (Fig. 2A), which is evidently due to melting and decomposition of this

Fig. 2. (A & B)—DTA Thermograms of Urea Complexes, Their Constituents and Mechanical Mixtures

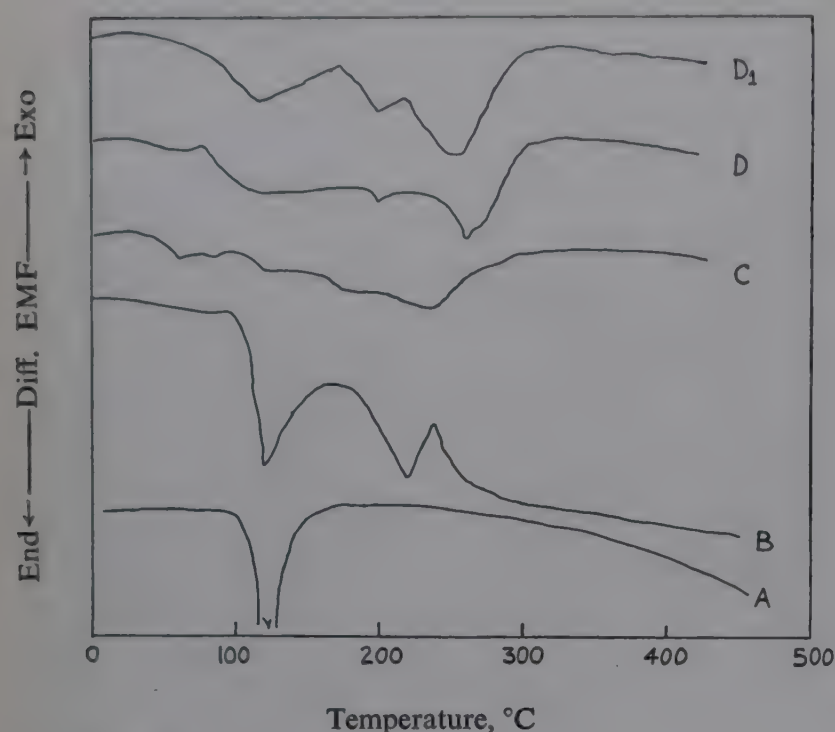


Fig. 2A—A—Urea
B—Urea-Nitrate
C—Urea-Ammonium Nitrate
D—Urea-Ammonium Chloride
D₁—Urea + Ammonium Chloride

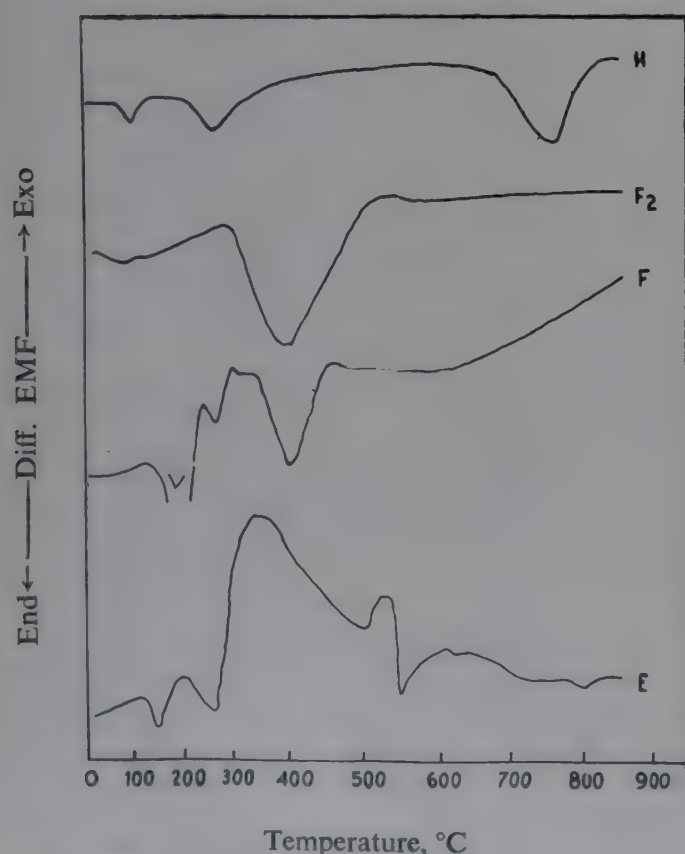


Fig. 2B—E—Urea-Calcium Nitrate
F—Urea-Dicalcium Hydrogen Phosphate
F₂—Dicalcium Hydrogen Phosphate
H—Urea-Phosphate

cal mixture (having similar composition) excepting one weak decomposition step at 60-100°C, which is absent in the later case (Fig. 1A). The weight-loss at 80°C has been found to be 2.9 per cent in this case. (Table 1). This step

is similar to that of urea nitrate and smell of ammonia is perceptible here also when kept at that temperature. The DTA thermogram reveals one weak endothermic peak at 60°C along with other peaks at 85°, 120°, 180°, 240° and 280°C (Fig. 2A). It is known that phase change of ammonium nitrate corresponding to $IV \rightleftharpoons III$, $III \rightleftharpoons II$ and $II \rightleftharpoons I$ takes place at 32, 84 and 125°C respectively and finally this compound melts at 170°C. The peaks at 85, 120 and 180°C are, therefore, due to phase changes (from III to I) and melting point of ammonium nitrate respectively, but the peak at 32°C corresponding to free ammonium nitrate is absent; instead, an additional peak at 60°C appears. This peak may be due to the decomposition of the recrystallized product. But as observed earlier, a DTA peak is not detectable to such small extent of decomposition by this apparatus. It may, therefore, be inferred that the peak appears at this temperature because of the combined effect of the decomposition and dissociation of this double salt.

Another indication in favour of dissociation is that the DTGA thermogram of the recrystallized product is similar to that of the mechanical mixture beyond this temperature (60°C). It may be mentioned here that the last two DTA peaks correspond to the decomposition steps occurring at 160-200 and 220-300°C in their DTGA thermograms. In the case of ammonium nitrate there is a sharp decomposition step at 180-300°C due to the complete decomposition of this compound yielding water vapour and nitrous oxide⁸ (Fig. 1A).

These two steps in both the cases are, therefore, due to decomposition of free urea and ammonium nitrate respectively. It is interesting to mention here that the weight loss at 350°C is 100 per cent like that of urea nitrate (Table 1).

DTGA thermogram of urea calcium nitrate complex shows six decomposition steps upto 850°C viz. at 60-100, 140-200, 200-350, 360-400, 460-500 and 700-750°C (Fig. 1B). Except the first step, endothermic peaks appear in all corresponding temperature ranges of the DTA thermogram (Fig. 2B). Here again, free ammonia has been found to escape at 60-100°C (wt. loss 1.5 per cent, Table 1). Although the nature of decomposition in other steps can not be assigned from these data, yet from the weight-loss value which is 87 per cent at 850°C, it is evident that all the nitrogenous component escapes when heated upto this temperature as a result of decomposition.

It is interesting to mention here that the decomposition characteristics of mechanically mixed urea and calcium nitrate tetrahydrate (prepared in agate mortar) is similar to that of their complex compound. It is worthwhile mentioning here that Lehr *et al*⁴ observed that complex

salt of these two components is also formed even when they are mechanically mixed in an agate mortar.

Urea-Ammonium Chloride System: The urea-ammonium chloride complex shows four decomposition steps viz. at 60-80, 150-200, 200-260 360°C, in its DTGA thermogram (Fig. 1A), the first one being very weak compared to the others. Although the DTGA thermogram of this complex is similar to that of the mechanical mixture (having similar molar composition) yet this weak step is absent in the latter case. Here again, smell of ammonia is perceptible at this temperature range and the loss in weight occurring at 80°C is 0.52 per cent compared to 0.05 per cent of the mechanical mixture. Again, DTA thermograms of both the complex compound as well as the mechanical mixture are similar and except the peak at 60-100°C., other peaks appear in the same temperature ranges where decomposition steps are recorded (Fig. 2A). It is known that ammonium chloride does not decompose but sublimes beyond 126°C and the sublimation increases with rise of temperature⁸. The step at 150-200°C is, therefore, due to decomposition of free urea whereas the higher ones for sublimation of ammonium chloride. It is, thus, event that the urea-ammonium chloride complex dissociates probably at 60-80°C and its decomposition characteristics at higher temperatures are similar to that of mechanical mixture; the non-existence of DTA peak at this temperature region may be due to the lesser extent of decomposition as compared to that of urea-ammonium nitrate complex.

Urea Phosphate and Urea-Dicalcium Hydrogen Phosphate System: There are four decomposition steps, viz. occurring at 60-100, 100-180, 200-280 and 650°C, respectively in the DTGA thermogram of urea phosphate (Fig. 1B). Except the first one which is very weak as compared to the others, endothermic peaks appear in the DTA thermogram at all corresponding temperatures where decomposition occurs (Fig. 2B). The loss in weight at 80°C is 1.8 per cent and smell of ammonia is perceptible at this temperature (Table 1). At 450°C the total weight-loss is 27 per cent, whereas at 850°C it is 98 per cent. It was observed visually that the product, when cooled after heating upto 850°C, is liquid and fumes strongly resembling that of phosphoric acid. It is, thus, quite probable that the nitrogenous constituents decompose at lower temperature and escape as gases leaving phosphoric acid at the higher temperature region.

The decomposition characteristics of urea-dicalcium hydrogen phosphate recrystallized product is similar to that of mechanical mixture (Fig. 1B). Thus, it indicates that there is no complex formation on recrystallization.

In the DTA thermogram of CaHPO_4 , two endothermic peaks appear at 100 and 410°C (Fig. 2B); the first one is weak and arises from the release of adsorbed moisture, while the second one is quite strong due to transformation⁴ of CaHPO_4 to $\text{Ca}_2\text{P}_2\text{O}_7$. There is also a corresponding decomposition step in the DTGA thermograms of urea-dicalcium phosphate samples (both recrystallized and the mechanical mixture). The initial step at 120-250°C is comparable to that of urea and may, therefore, be ascribed as to the decomposition of free urea at that temperature range. But this step is double-natured having one decomposition maximum at 140°C. This may arise from the reaction of urea and CaHPO_4 when ammonia is set free (as confirmed by smelling) and CaNH_4PO_4 is formed. The step which appears at 250-380°C is, therefore, due to the decomposition of this compound and that at about 400°C is for CaHPO_4 . Again the weight-loss of this sample at 450°C is 52 per cent, after which it remains constant even when heated upto 850°C (Table 1). This confirms that the product of decomposition is mainly $\text{Ca}_2\text{P}_2\text{O}_7$.

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This paper deals with the chemical examination of several rock phosphate samples and x-ray identification of various phases present in them which were subjected to different degrees of sulphuric acid treatment. A comparative study of physico-chemical properties of the resultant single super-phosphates as regards the suitability of the different Indian rock phosphates for superphosphate production is also given. The factors involved in the reaction of different rock phosphates with the acid have been assessed, and their P_2O_5 availability index was determined to get an idea of the suitability of the resultant superphosphates as economic phosphate sources in crop plant nutrition.

A Study on the Acidulation of Indian Rock Phosphates In the Preparation of Single Superphosphates

By S. C. CHATTERJEE, A. K. SIRCAR AND S. K. GHOSH,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

It is generally known in superphosphate technology that the nature of phosphatic rock, degree of fineness to which it is ground, concentration of sulphuric acid used, the proportion in which the acid and rock are mixed and the temperature of reaction influence the properties of superphosphates so prepared.

Many Indian rock phosphates are of igneous origin. However, the recently reported sedimentary phosphate deposits by G.S.I.* Indian rock phosphate deposits of igneous and sedimentary origin have been found² to vary widely in nature and they contain apatite minerals along with other associated minerals, iron oxides, clay, calcite, dolomite and quartz as impurities. A systematic study was, therefore, made to see the reactions of such rocks with varying concentrations of sulphuric acid in the preparation of superphosphates and to assess the economy and suitability of such superphosphates in crop plant nutrition.

Experimental

The Indian rock phosphates selected for this investigation were (1) Vizag (Andhra Pradesh), (2) Jaisalmer (Rajasthan), (3) Kimoi (U.P.) (4) Mussorie (U.P.) and (5) Ramchandrapahar (Bihar). Of these, numbers 1 and 5 are of igneous origin and the rest were sedimentary.

Along with these five phosphates, a sample of imported

rock phosphate from Jordan was also included in this study for comparison: its details and behaviour with sulphuric acid have been reported earlier³.

All the Indian rock phosphates were finely ground and passed through 100 mesh sieve (B.S.S.) before starting the experiment. Their physico-chemical properties are given in Tables 1 and 2.

Acid Treatment of Rock Phosphates: 10 g. of each of these finely ground rock phosphates were treated with 0, 30, 60, 90 and 120 per cent by weight of sulphuric acid (sp.gr. 1.50), according to the procedure described earlier⁴. The physico-chemical properties of these acidulated rock samples are presented in Tables 3 and 4.

X-ray Diffraction Analysis: All the samples were studied by the x-ray diffraction technique for the identification of the phases formed due to acid treatment. For this the x-ray diffraction patterns of all the acid-treated and untreated samples were obtained in a Guinier camera with $CuK\alpha$ radiation at 40 KV and 20 mA, giving 6-8 hours exposure to each sample. The results of x-ray diffraction analysis are presented in Tables 2 and 3.

Results and Discussion

The behaviour of different rock phosphates at varying concentrations of sulphuric acid in converting rock phosphates to water-soluble and 'available' (water-soluble and citrate-soluble) phosphates is shown in

*Geological Survey of India.

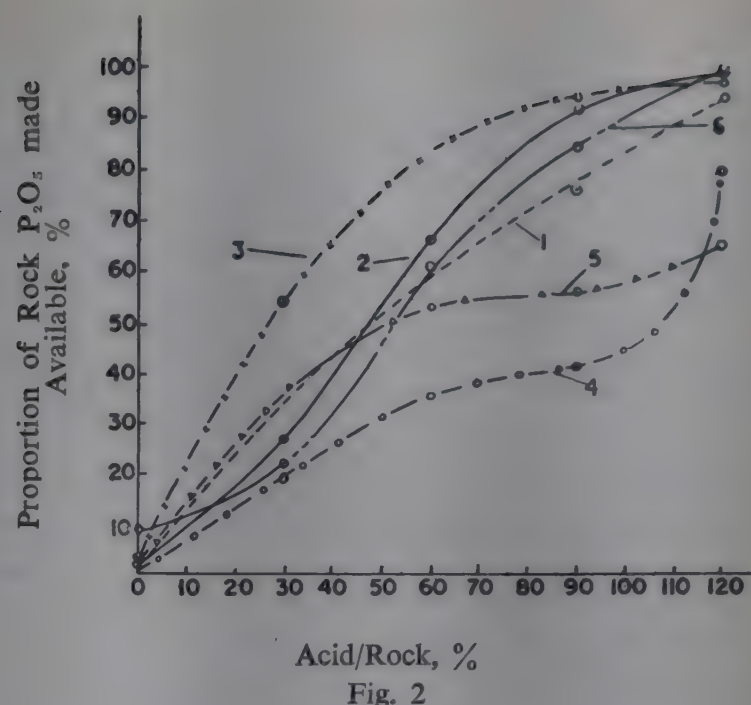
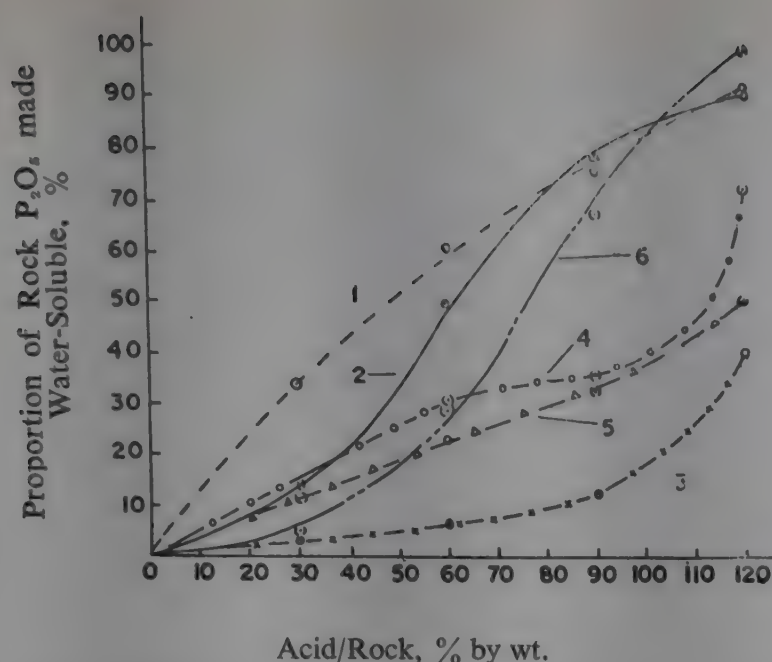


Fig. 1—Behaviour of Rock Phosphates in Sulphuric Acid

1. Vizag
2. Jaisalmer
3. Kimoi
4. Mussorie
5. Ramchandrapahar
6. Jordan

Figs. 1 & 2 respectively. On comparison of Figs. 1 & 2, it is observed that with increased acid concentration the proportion of rock phosphate made water-soluble and available P_2O_5 is more in Jordan, Vizag and Jaisalmer samples than in those from Mussorie, Ramchandrapahar and Kimoi. However, Kimoi shows high available P_2O_5 content after acid reaction. A comparison amongst

Jordan, Vizag and Jaisalmer samples reveals that below 30 per cent sulphuric acid addition by weight in Jaisalmer and Jordan, there is not much change in the proportion of rock P_2O_5 made water-soluble or “available”, while there is a sharp increase in the same with the increased addition of sulphuric acid upto 100 per cent by weight. On the other hand, in Vizag sample the initial addition of sulphuric acid shows a gradual increase in the proportion of rock phosphate (P_2O_5)

TABLE 1—PHYSICO—CHEMICAL PROPERTIES OF ROCK PHOSPHATES

Sl. No.	Name of Sample	Total P_2O_5 , %	Citrate-soluble P_2O_5 , %	SiO_2 , %	CaO , %	R_2O_3 , %	CO_2 , %
1.	Vizag Rock Phosphate	36.8	—	0.4	54.6	7.9	1.5
2.	Jaisalmer Rock phosphate	26.5	0.5	5.0	48.7	5.0	12.8
3.	Kimoi Rock Phosphate	29.4	0.9	2.9	31.1	25.0	1.8
4.	Mussorie Rock Phosphate from Paritibba	15.0	—	8.4	50.9	4.5	6.5
5.	Ramchandrapahar Rock Phosphate	24.2	0.5	6.2	30.6	20.0	—
6.	Jordan Rock Phosphate	34.5	—	2.5	52.4	0.2	4.8

TABLE 2—X-RAY DIFFRACTION ANALYSIS, OF ROCK PHOSPHATES

Sl. No.	Name of Sample	Major Phase	Minor Phase	Remarks
1.	Vizag Rock Phosphate	Francolite	—	Least substitution by CO_3^{2-}
2.	Jaisalmer Rock Phosphate	Francolite	$CaCO_3$, Quartz	Maximum substitution by CO_3^{2-}
3.	Kimoi Rock Phosphate	Francolite	Quartz, Biotite	Least substitution by CO_3^{2-}
4.	Mussorie Rock Phosphate	Francolite, Quartz	Dolomite, Biotite	Less substitution by CO_3^{2-}
5.	Ramchandrapahar Rock Phosphate	Fluoroapatite	Hydrated oxides of iron, Biotite, variscite and quartz	Pure fluoroapatite
6.	Jordan Rock Phosphate	Francolite	$CaCO_3$	Appreciable amount of substitution by CO_3^{2-}

TABLE 3—X-RAY DIFFRACTION ANALYSIS OF ROCK PHOSPHATE SAMPLES & THEIR ACIDULATED PRODUCTS

Sl. No.	Name of Rock Phosphate	0% Acid/Rock by weight, Rock Phosphate		30% Acid/Rock by weight			60% Acid/Rock by weight		
		Major	Minor	Major	Minor	Trace	Major	Minor	Trace
		1	2	3	4	5	6	7	8
1.	Vizag Rock Phosphate	Francolite	—	Apatite	Mono-calcium phosphate mono-hydrate, Calcium sulphate hemihydrate	Dicalcium phosphate dihydrate Quartz.	Mono-calcium phosphate mono-hydrate, Calcium sulphate hemihydrate	Dicalcium phosphate dihydrate	Apatite Quartz.
2.	Jaisalmer Rock Phosphate	Francolite	CaCO ₃ , Quartz	Apatite	Calcium sulphate hemihydrate, Dicalcium phosphate dihydrate, Monocalcium phosphate monohydrate	Quartz	Calcium sulphate hemihydrate	Dicalcium phosphate dihydrate Monocalcium phosphate monohydrate, Apatite	Quartz
3.	Kimoi Rock Phosphate	Francolite	Quartz, Biotite	Apatite	Calcium sulphate hemi-hydrate, Iron-Aluminium sulphate hydrate, Dicalcium phosphate dihydrate	Quartz	Dicalcium phosphate dihydrate, Calcium sulphate hemihydrate	Apatite, Iron-Aluminium Sulphate hydrate	Mono-Calcium phosphate mono-hydrate Quartz
4.	Mussorie Rock Phosphate	Francolite and Quartz	Dolomite, Biotite	Apatite	Magnesium sulphate hydrate, Calcium sulphate hemi-hydrate, Quartz.	Dicalcium phosphate dihydrate, Mono-calcium phosphate mono-hydrate	Apatite	Mono-calcium phosphate mono-hydrate, Calcium sulphate hemi-hydrate, Magnesium sulphate hydrate	Dicalcium phosphate dihydrate Quartz.
5.	Ramchandra-pahar Rock Phosphate	Fluoro-apatite	Hydrated oxides of Iron, Biotite, Variscite, & Quartz.	Apatite	Dicalcium phosphate dihydrate	Mono-calcium phosphate mono-hydrate, Calcium sulphate hemi-hydrate, Quartz, Iron-Aluminium Sulphate hydrate	Apatite	Calcium sulphate hemi-hydrate, Dicalcium phosphate dihydrate, Iron-Aluminium sulphate hydrate	Mono-calcium phosphate mono-hydrate Quartz.
6.	Jordon Rock Phosphate	Francolite	CaCO ₃	Apatite	Dicalcium phosphate dihydrate, Calcium sulphate hemihydrate	Quartz.	Apatite Dicalcium phosphate dihydrate	Mono-calcium phosphate mono-hydrate, Calcium sulphate hemicydrate	Quartz.

TABLE 3—X-RAY DIFFRACTION ANALYSIS OF ROCK PHOSPHATE SAMPLES & THEIR ACIDULATED PRODUCTS—(Contd.)

Sl. No.	Name of Rock Phosphate	90% Acid/Rock by weight			120% Acid/Rock by weight		
		Major	Minor	Trace	Major	Minor	Trace
		9	10	11	12	13	14
1.	Vizag Rock Phosphate	Monocalcium phosphate mono-hydrate Calcium sulphate hemihydrate	Dicalcium phosphate dihydrate	Apatite Quartz	Monocalcium phosphate mono-hydrate, Calcium sulphate hemihydrate		Dicalcium phosphate dihydrate Quartz
2.	Jaisalmer Rock Phosphate	Monocalcium phosphate mono-hydrate, Calcium Sulphate hemi-hydrate	Dicalcium phosphate dihydrate	Apatite Quartz	Monocalcium phosphate mono-hydrate, Calcium sulphate hemi-hydrate		Dicalcium phosphate dihydrate Quartz
3.	Kimoi Rock Phosphate	Dicalcium phosphate dihydrate, Calcium Sulphate hemihydrate	Monocalcium phosphate mono-hydrate, Iron-Aluminium sulphate hydrate	Apatite Quartz	Monocalcium phosphate mono-hydrate, Calcium sulphate hemi-hydrate, Dicalcium phosphate dihydrate	Iron-Aluminium Sulphate hydrate	Quartz
4.	Mussorie Rock Phosphate	Apatite, monocalcium phosphate monohydrate, Calcium sulphate hemihydrate	Magnesium sulphate hydrate	Dicalcium phosphate dihydrate, Quartz	Monocalcium phosphate mono-hydrate, Calcium sulphate hemihydrate	Magnesium sulphate hydrate, Dicalcium phosphate dihydrate, Quartz	Apatite
5.	Ramchandrapahar Rock Phosphate	Calcium sulphate hemihydrate, Dicalcium phosphate dihydrate	Apatite, Monocalcium phosphate monohydrate, Iron-Aluminium sulphate hydrate	Quartz	Monocalcium phosphate monohydrate, Calcium sulphate hemihydrate	Dicalcium phosphate dihydrate, Iron-Aluminium sulphate hydrate	Apatite Quartz
6.	Jordon Rock Phosphate	Monocalcium phosphate monohydrate	Dicalcium phosphate dihydrate, Calcium sulphate, hemihydrate, Apatite	Quartz	Monocalcium phosphate monohydrate	Calcium sulphate hemihydrate	Quartz

TABLE 4—CHEMICAL ANALYSIS OF ACID-TREATED ROCK PHOSPHATES

Sl. No.	Acid/Rock Percent by Weight	Vizag Rock Phosphate			Jaisalmer Rock Phosphate			Mussorie Rock Phosphate			Kimoi Rock Phosphate			Ramchandrapahar Rock Phosphate		
		Water-soluble P ₂ O ₅ , %	Avail-able P ₂ O ₅ , %	Total P ₂ O ₅ , %	Water-soluble P ₂ O ₅ , %	Avail-able P ₂ O ₅ , %	Total P ₂ O ₅ , %	Water-soluble P ₂ O ₅ , %	Avail-able P ₂ O ₅ , %	Total P ₂ O ₅ , %	Water-soluble P ₂ O ₅ , %	Avail-able P ₂ O ₅ , %	Total P ₂ O ₅ , %	Water-soluble P ₂ O ₅ , %	Avail-able P ₂ O ₅ , %	Total P ₂ O ₅ , %
1.	0 Rock Phosphate	0.0	0.0	36.8	0.0	0.5	26.5	0.0	0.0	15.0	0.0	0.9	29.4	0.0	0.5	24.2
2.	30	10.3	12.1	30.1	3.0	6.0	22.1	1.8	2.3	12.4	0.7	13.1	24.4	2.3	6.9	19.8
3.	60	16.3	17.9	26.9	10.1	13.3	20.3	3.5	4.0	11.3	1.4	17.7	21.4	3.9	9.2	17.3
4.	90	19.1	20.0	25.1	14.5	17.0	18.4	3.9	4.4	10.8	2.3	17.9	19.1	5.1	8.6	15.4
5.	100	20.9	21.8	22.5	16.1	17.5	17.7	7.6	8.3	10.4	7.6	18.0	18.4	6.7	8.5	13.1

made water-soluble or available, and this rate remains almost unaltered up to the addition of 90 per cent by weight of sulphuric acid beyond which the rate does not increase, but ultimately the whole of rock phosphate (P_2O_5) is converted to water-soluble phosphate.

Mussorie, Ramchandrapahar and Kimoi rock phosphates show a typical behaviour in the conversion of rock phosphate to water-soluble and available phosphate, when acid was added in different concentrations.

The addition of sulphuric acid to Mussorie rock phosphate shows an appreciable increase in the amount of conversion of rock phosphate (P_2O_5) to water-soluble and available phosphate at acid concentrations upto 60 per cent by weight sulphuric acid, thereafter it remains constant upto 90 per cent by weight of sulphuric acid addition, while there is a sharp increase in conversion rate with further addition of acid.

Ramchandrapahar rock phosphate shows a slow conversion rate, and attains nearly 60 per cent conversion at the highest level of acid application i.e. 120 per cent sulphuric acid by weight.

Kimoi rock phosphate shows an interesting behaviour when acid was added to convert rock phosphate (P_2O_5) to water-soluble and available phosphates. While the proportion of rock phosphate made water-soluble is only 40 per cent at the highest level of sulphuric acid addition, the proportion of rock phosphate (P_2O_5) made 'available' reaches almost upto 95 per cent conversion at an acid concentration of only 90 per cent acid/rock by weight. The proportion of rock phosphate made water-soluble is noticeable only after addition of 60 per cent acid/rock by weight, whereas the proportion of rock phosphate made available increases sharply with the initial addition of sulphuric acid and remains unaltered upto 60 per cent acid/rock by weight.

A critical survey of the results discussed earlier reveals that the water- and citrate-solubility of the acid-treated rock phosphates is dependent on the physical characteristics of the parent rock. Most of the rock phosphates are substituted by carbonate ion in varying amounts with the exception of Ramchandrapahar sample; Vizag rock phosphate is almost a pure apatite. The other samples contain varying degrees of free calcite, dolomite, sesquioxides and clay minerals as impurities (Table 1 & 2). Basing on these observations, the behaviour of the individual rocks as regards their acidulation characteristics are discussed one by one.

The low conversion rate of Jordan, Jaisalmer and Mussorie rock phosphates at less acid concentration may be due to the presence of free calcite and dolomite in

them. The abrupt increase in conversion rate in Mussorie rock phosphate at an acid concentration 90 per cent, sulphuric acid by weight indicates that the free acid starts reacting with the apatite crystals left at this stage.

The nonconformity regarding the conversion rate of the rock phosphate to water-soluble and available phosphate in the case of Kimoi rock phosphate is due to the presence of high amounts of sesquioxide in the superphosphates prepared, causing low water and high citrate-solubility, which is in conformity with Lehrecke's observation⁴.

In the case of Ramchandrapahar sample, the acid treatment does not show appreciable increase in conversion of rock phosphate to water-soluble or available phosphate. The impurities present in this rock phosphate are more active in consuming acid thereby leaving less acid for the rock to react with. The difference in the behaviour regarding the proportion of rock phosphate made water-soluble or available, between Kimoi and Ramchandrapahar rocks, clearly shows that the former sample is more reactive than the latter and hence is giving rise to high conversion of rock phosphate to available P_2O_5 in presence of acid, although it contains higher sesquioxide and carbon dioxide (Table 1) than the Ramchandrapahar sample. The x-ray results (Tables 2 & 3) also corroborate this fact.

Visual observations showed that superphosphates prepared from Ramchandrapahar, Mussorie and Kimoi rock phosphates were wet and sticky. Chemical tests after the reaction period showed the presence of free sulphuric acid in the Ramchandrapahar sample even at 60 per cent acid/rock by weight and this increases as the percentage of acid increases. The stickiness in the superphosphates prepared from these samples may be due to the presence of clay minerals in them (Table 2).

The x-ray diffraction study of the acid-treated rock phosphates (Table 3) show that (a) in Vizag sample the presence of monocalcium phosphate is noticeable from the initial dose of acid addition, (b) in Jaisalmer sample the same is observed after 30 per cent acid/rock and in Kimoi and Mussorie samples after 60 per cent acid/rock by weight and (c) the Ramchandrapahar sample shows a little formation of monocalcium phosphate along with iron-aluminium sulphate from the initial acid dose itself and it increases at an higher acid concentration. From the above it appears that the conversion of rock phosphate to water-soluble and available phosphate is different in different samples. This may be due to the fact that as the acid concentration was increased, the available surface became more open for the solvent to react with the rock phosphate which was previously

blocked by the impurities present in the parent rock. Because of this, the rock phosphate having such impurities consumes more acid for the same amount of conversion.

Jordan, Vizag and Jaisalmer rock phosphates, after treatment with sulphuric acid, form superphosphates of a very good quality even at low acid concentrations. Of the three sources, Jordan rock phosphate and its acidulated product were intensively studied earlier⁵ in the green-house and the latter was found to be highly efficient in supplying phosphates to plants. Even the superphosphate prepared by adding 60 per cent by weight sulphuric acid gave better results than other superphosphates having 100 per cent water-soluble phosphates. From this it appears that the superphosphate prepared from Vizag and Jaisalmer rock phosphates, because of their similarity in the availability index (Table 4), might be an efficient phosphatic source for crop plant nutrition at a low cost.

Superphosphates prepared from Kimoi rock phosphate should be a good source of citrate-soluble phosphate in crop plant nutrition.

Ramchandrapahar and Mussorie rock phosphates show low water-soluble and available phosphate even

at high acid concentrations. If the impurities present as clays, hydrated oxides of iron and aluminium in Ramchandrapahar rock phosphate, and dolomite in Mussorie rock phosphate could be separated by physical methods, these rock phosphates might also produce good quality superphosphates at low cost.

Further work regarding the P_2O_5 availability of Indian rock phosphates for plant nutrition and improvement in the quality of superphosphates obtainable there-from is in progress.

Acknowledgement

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The influence of the nature and content of the reacting agents on the formation of the intermediate $[\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4]$ has been discussed. Further, this study embraces detailed work on the characterization of the thermally decomposed product and crystallographic properties of cupric chromite (CuCr_2O_4) and the intermediate product, $[\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4]$.

Studies on the $\text{CuO}-\text{Cr}_2\text{O}_3$ System

By B. SANDILYA, AJIT ROY AND S. K. GHOSH,

*Planning and Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Introduction

Copper-chromium oxide catalysts are generally used for hydrogenation and dehydrogenation reactions. It has been shown by previous workers that its activity depends very much on the method of preparation, intermediate products, temperature and the duration of ignition.

Various attempts were made to characterize the composition of the intermediates obtained by different methods which are dependent on various factors, like the concentrations of ammonia and copper salt and amount of potassium dichromate, but no definite conclusion has yet been reached. Some observations on the heat-treated products of the intermediate at different temperatures are already available in the literature^{1,2}. But the nature of the heat-treated products, prepared at varying $\text{CuO}:\text{NH}_3$ ratio, has not been studied at all.

There is much confusion about the crystal structure of cupric chromite and different views were expressed³. Further, nothing is known about the crystal structure of the intermediate product, $\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$.

The purpose of the present study is, therefore, to investigate in more details the complex nature and the variables of the reaction leading to the formation of the intermediate, characterization of its different heat-treated products of varying thermal history and the crystallographic properties of the intermediate and cupric chromite, which may throw some light on the behaviour of copper oxide-chromium oxide catalyst.

EXPERIMENTAL

A. Preparation of Samples

(i) *Preparation of Intermediates*: The method adopted

here is the recent one developed by Calingaert *et al*⁴, which is a slight modification of that given by Adkins *et al*⁵ and Lazier⁶. An intermediate compound is precipitated by the reaction of copper sulphate with potassium dichromate and aqueous ammonia. Keeping the dichromate concentration constant, the mole ratio of $\text{CuO}:\text{NH}_3$ was varied from 1:7 to 1:18 and the precipitate obtained in each case varied in colour—from greenish brown to deep brown. The precipitates were washed repeatedly with distilled water and finally dried. The three samples, thus obtained, were designated as A, B and C.

(ii) *Preparation of Cupric Chromite (CuCr_2O_4)*: The precipitate A ($\text{CuO}:\text{NH}_3$ is 1:7) obtained from above was roasted at about 500°C for about 2 hours. The finely divided black substance obtained was leached with warm-concentrated hydrochloric acid and allowed to stay overnight for complete dissolution of the phases other than cupric chromite and to settle the finer particles of cupric chromite. Filtration, repeated washing, first with concentrated hydrochloric acid and then with distilled water combined with subsequent drying gave the desired product, which was designated as D.

B. Heat Treatment of Intermediates

The precipitates B ($\text{CuO}:\text{NH}_3=1:12.25$) and C ($\text{CuO}:\text{NH}_3$ 1:18) obtained from (i), after washing and drying, was heated at different temperatures ranging from 200 to 1000°C for 2 hours and the heated products were kept for analysis.

C. X-ray Analysis

X-ray photographs of all the samples, mainly A, B, C

TABLE 1—PHASES PRESENT IN SAMPLES

Sl. No.	Samples	Crystalline Phases Present	
		Major	Minor
1.	A(CuO:NH ₃ = 1:7)	Cu(OH)NH ₄ CrO ₄ ·	
2.	B(CuO:NH ₃ = 1:12.25)	Cu(OH)NH ₄ CrO ₄	CuSO ₄ ·3 Cu(OH) ₂
3.	C(CuO:NH ₃ = 1:18)	CuSO ₄ ·3Cu(OH) ₂	Cu(OH)NH ₄ CrO ₄

(Intermediates) and D (Cupric chromite) and the heat-treated products, were taken in a Guinier camera using CuK α radiation, X-ray tube running at 40 KV and 20 mA. MoK α radiation using zirconium filter was used for taking powder photograph in Debye-Scherrer camera (rad.-11.46 cm) for the sample D. The d-spacings were calculated accurately and the phase identification was done by the method of Hanawalt *et al*⁷.

Results

The phases present in the prepared samples (intermediates) A, B and C, as revealed by x-ray diffraction technique, are shown in Table 1. The 'd' spacings of these samples are given in Table 2.

The x-ray diffraction pattern of the sample D revealed the presence of pure cupric chromite (CuCr₂O₄). The 'd' spacings of the sample along with A.S.T.M. data are given in Table 3.

The phases present in the heat-treated samples of intermediates B(CuO:NH₃=1:12.25) and C (CuO:NH₃=1:18) are shown in Tables 4 and 5.

Discussion

Different points of view regarding the composition of the intermediates during the preparation of copper chromite catalyst have been expressed. As such, there are still some uncertainties regarding its exact composition and the optimum conditions most suitable for its preparation.

However, Calingaert *et al*⁴ have shown that the reaction occurs during its preparation in the following way:

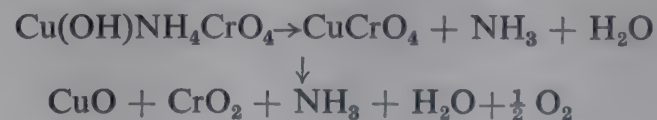
$$\text{CuSO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + 4\text{NH}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Cu(OH)NH}_4\text{CrO}_4\text{(PPT)} + \text{K}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4 \quad (1)$$

Recently, Stammers *et al*² have put forward the view that the composition of the precipitate depends very much on the initial ammonia concentration and, in some

cases, on the copper ion concentration, which led them to believe that complexes of the type [Cu(NH₃)_n]²⁺ for n=1 to 5 might be forming.

In the present work, it has been observed that with increasing ammonia concentration, the major phase is the basic copper sulphate with decreasing amounts of Cu(OH)NH₄CrO₄, which suggests that the main reaction taking place at high ammonia concentration is probably as follows: 4CuSO₄ + 6NH₃ + 6H₂O → CuSO₄·3Cu(OH)₂ + 3(NH₄)₂SO₄. (2), whereas reaction (1) takes place to a very small extent. At low ammonia concentration, the reaction takes place at one step leading to the formation of Cu(OH)NH₄CrO₄(PPT) via reaction (1).

The optimum limit of CuO:NH₃ mole ratio for the formation of the pure Cu(OH)NH₄CrO₄ is about 1:7. It is worthwhile mentioning here the decomposition of pure Cu(OH)NH₄CrO₄ at different temperatures, as has been reported in the literature. Stroupe¹ has observed that the decomposition of pure Cu(OH)NH₄CrO₄ between 300 and 350°C gives amorphous copper-chromium oxide, while at about 500°C finely divided black crystalline cupric chromite is formed, which changes to cuprous chromite with increasing temperature and is completely converted to cuprous chromite at 1100°C. However, Stammers *et al*² has stated that at a lower temperature, a second reaction probably occurs according to the following equation:



In the present case, the behaviour of the intermediates B and C, which initially contain both Cu(OH)NH₄CrO₄ and CuSO₄·3Cu(OH)₂, towards heat treatment is very much complicated as can be seen from Tables 1 and 5.

In case of intermediate B, the major phase Cu(OH)NH₄CrO₄ exists upto 400°C. At 200°C, presence of a

TABLE 2—X-RAY DATA OF THE INTERMEDIATE PREPARED WITH VARYING $\text{CuO}:\text{NH}_3$ RATIO

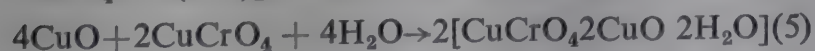
Intermediate I $\text{CuO}:\text{NH}_3=1:7$ (Mole ratio)		Intermediate II $\text{CuO}:\text{NH}_3=1:12.25$ (Mole ratio)		Intermediate III $\text{CuO}:\text{NH}_3=1:18$ (Mole ratio)		$\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$ J.A.C.S. 49—71 (571)		$\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ A.S.T.M. 3—0282 Brochantite	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
7.1	s	7.1	s	7.1	m	7.1	100	—	—
		6.5	vvw	6.5	ms	—	—	6.5	67
		5.4	vvw	6.0	vvw	—	—	—	—
4.97	vw	5.0	vw	5.4	ms	—	—	5.4	58
		3.91	vvw	5.0	vw	4.96	10	4.96	3
				3.91	s	—	—	3.91	100
3.69	ms	3.70	ms	3.70	vw	3.69	40	—	—
		3.55	vvw	3.60	vw	—	—	—	—
3.28	s	3.30	s	3.21	ms	3.28	55	3.32	7
2.95	m	2.96	ms	2.95	ms	2.945	15	3.20	42
				2.89	vvw	—	—	2.94	20
2.72	ms	2.74	ms	2.70	ms	2.737	25	2.69	50
2.61	m	2.62	m	2.62	m	2.622	20	—	—
2.54	ms	2.55	m	2.56	w	2.542	30	—	—
				2.51	s	—	—	2.53	67
2.49	vvw	2.50	vvw	2.46	m	—	—	2.46	10
		2.46	vvw	2.39	w	2.365	10	2.39	7
				2.32	vvw	—	—	—	—
2.30	vvw	2.30	w	2.30	w	2.304	20	2.29	13
2.20	vvw	2.20	vw	2.20	w	—	—	2.19	13
				2.15	w	—	—	2.12	3
				2.13	w	—	—	—	—
				2.10	w	—	—	—	—
				2.03	vw	—	—	2.07	10
				1.98	w	—	—	2.01	7
1.958	w(Br)	1.96	w(Br)	1.96	vw	1.962	10	1.96	13
				1.90	vvw	—	—	1.89	3
1.84	w	1.84	w	1.84	w	1.848	5	—	—
1.83	vw	1.82	w	1.81	vw	1.832	5	1.82	17
1.76	w	1.78	w	1.75	ms	1.774	15	1.74	33
		1.75	vw	1.72	vw	—	—	—	—
1.70	vvw	—	—	1.69	vw	—	—	1.67	10
1.65	vw	1.66	vvw	1.65	vw	1.645	15	1.64	13
1.63	w	—	—	1.61	vvw	—	—	1.60	13
				1.57	w	—	—	—	—
1.54	w(Br)	1.545	vw	1.55	w	1.545	10	1.56	23
				1.538	w	—	—	1.53	20
				1.56	vw	—	—	1.51	20
1.475	w(Br)	1.48	w(Br)	1.475	vvw	1.483	10	1.46	17
1.445	vvw	1.45	vvw	1.445	vw	1.456	5	1.44	17
1.38	vw	—	—	1.400	vw	1.383	5	1.40	17
1.325	vvw	1.35	vvw	1.355	vvw	1.315	5	1.37	10
		1.31	vvw	1.315	vvw	1.285	5	1.31	20
1.275	vvw	—	—	—	—	—	—	1.28	13
1.249	vvw	—	—	—	—	—	—	—	—
1.145	vw	—	—	—	—	1.143	5	—	—

TABLE 3—X-RAY DATA OF CUPRIC CHROMITE

CuCr ₂ O ₄ (prepared)		CuCr ₂ O ₄ (A.S.T.M.) 5-0657	
dÅ	I	dÅ	I
4.77	mw	4.87	(15)
3.88	w		
3.00	w	3.017	(25)
2.874	m (Br)	2.874	(35)
2.55	s	2.556	(100)
2.40	ms	2.401	(60)
2.128	w	2.134	(25)
1.949	vw	1.96	(10)
1.710	vw	1.706	(15)
1.633	ms	1.629	(40)
1.592	vvw	1.589	(15)
1.503	m	1.505	(30)
1.442	ms	1.442	(40)
1.299	vvw	1.293	(5)
1.274	m	1.276	(15)
1.252	vvw		
1.192	vvw	1.195	(5)
1.108	vw		
1.065	vw		
0.983	vvw		
0.955	vvw		
0.938	vvw		
0.891	vw		
0.855	vw		

new phase CuCrO₄. 2CuO 2H₂O is observed which no longer exists at 400°C. The basic copper sulphate is seen to exist upto 200°C beyond which it decomposes to copper oxide. At 300°C copper chromate (CuCrO₄) is one of the major phases which does not exist at higher temperature. At 400°C, the presence of cupric chromite is observed, which increases upto 600°C; the formation of cuprous chromite starts at about 800°C and the conversion of cupric to cuprous chromite is complete at 1000°C. The whole change can schematically be represented as follows:

At about 200°C or below, partial decomposition of Cu(OH)NH₄CrO₄ takes place forming CuCrO₄. At the same time CuO produced by decomposition of basic copper sulphate combines with CuCrO₄ to form CuCrO₄. 2CuO 2H₂O.



At about 300°C, most of the residual Cu(OH)NH₄CrO₄ decomposes to form CuCrO₄ according to the reaction (3)

TABLE 4—THE PHASES PRESENT IN SAMPLE B

Temp. of Heating, °C	Phases Present and Relative Amounts as Determined by X-ray Intensity		
200	Cu(OH)NH ₄ CrO ₄	Major	
	CuCrO ₄ 2CuO 2H ₂ O	Minor	
	CuSO ₄ 3 Cu(OH) ₂	Trace	
300	CuCrO ₄	Major	Almost in equal-amounts
	CuO	Major	
	Cu(OH)NH ₄ CrO ₄	Minor	
	CuCrO ₄ 2CuO 2H ₂ O	Trace	
400	CuO	Major	Amount increased than that at 300°C
			Amorphous nature
	CuCr ₂ O ₄	Minor	
	Cu(OH)NH ₄ CrO ₄	Trace	
500	CuO	Major	Almost same in amount as that at 400°C but well crystallised
	CuCr ₂ O ₄	Minor	Slightly greater in amount than that at 400°C but well crystallised
600	CuO	Major	Almost same as that at 500°C
	CuCr ₂ O ₄	Major	Slightly greater in amount than that at 500°C
700	CuO	Major	The amount is same as that at 600°C
	CuCr ₂ O ₄	Major	
			Both CuO and CuCr ₂ O ₄ are better crystallised than that at 500°C & 600°C
800	CuO	Major	The amount is slightly less than that at 700°C
	CuCr ₂ O ₄	Major	
	Cu ₂ Cr ₂ O ₄	Trace	
900	Cu ₂ Cr ₂ O ₄	Major	
	CuO	Minor	
	CuCr ₂ O ₄	Trace	
1000	Cu ₂ Cr ₂ O ₄	Major	
	CuO	Minor	Less than that at 900°C
	CuCr ₂ O ₄	Nil	

TABLE 5—PHASES PRESENT IN THE SAMPLE C

Temp. of Heating, °C	Phases Present and Relative Amounts as Determined by X-ray Intensity	
200	CuO	Major
	CuSO ₄ 3Cu(OH) ₂	Minor
	CuCrO ₄ ·2CuO 2H ₂ O	Trace
300	CuO	Major
	CuSO ₄ 3Cu(OH) ₂	Minor
	CuCrO ₄ 2CuO 2H ₂ O	Minor
	CuCr ₂ O ₄	Trace
400	CuO	Major
	CuCrO ₄ 2CuO 2H ₂ O	Major
	CuCr ₂ O ₄	Minor
	CuSO ₄ ·3Cu(OH) ₂	Trace
500	CuO	Major
	CuCrO ₄ 2CuO 2H ₂ O	Comparatively less than that at 400°C
	CuCr ₂ O ₄	Greater than that at 400°C
600	CuO	Major
	CuCr ₂ O ₄	Major Slightly greater than that at 500°C
700	CuO	In increased amount than that at 500°C
	CuCr ₂ O ₄	Slightly less than that at 500°C
	Cu ₂ Cr ₂ O ₄	Nil
800	CuO	Slightly less than that at 700°C
	CuCr ₂ O ₄	Very small
	Cu ₂ Cr ₂ O ₄	Appreciable
900	CuO	Almost same as that at 800°C
	CuCr ₂ O ₄	Trace
	Cu ₂ Cr ₂ O ₄	Almost same as that at 800°C
1000	CuO	Much less than that at 900°C
	CuCr ₂ O ₄	Nil
	Cu ₂ Cr ₂ O ₄	Much greater in amount than that at 900°C

and CuCrO₄ 2CuO 2H₂O also decomposes as: CuCrO₄·2CuO 2H₂O → CuCrO₄ + 2CuO + 2H₂O (6)

Cupric chromite is formed probably according to the following reactions:

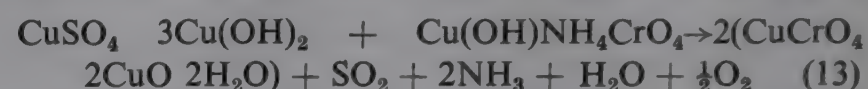
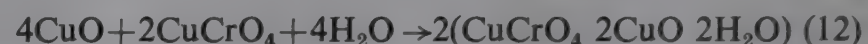
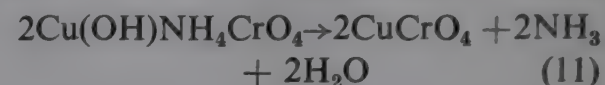


The formation of cuprous chromite occurs around 800°C as follows: CuCr₂O₄ + CuO → Cu₂Cr₂O₄ + (O) (9)

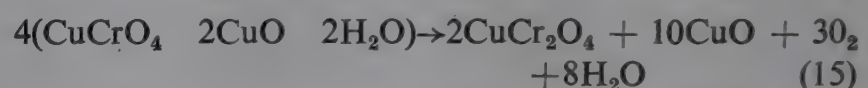
The behaviour of intermediate C is slightly different from that of B mainly, because in this case major phase is the basic copper sulphate which exists upto 400°C. In contrast to that of B, CuCrO₄ 2CuO 2H₂O is the major phase at 400°C which no longer exists above 500°C. Cupric chromite starts formation at about 300°C and increases in amount upto 500°C, above which it decreases gradually and disappears completely at 1000°C.

The changes occurring in case of C during the course of heating from 300 to 1000°C can probably be explained accordingly.

At low temperatures CuSO₄ 3Cu(OH)₂ → 4CuO + 3H₂O
i.e. around 300°C $+ \frac{1}{2}\text{O}_2 + \text{SO}_2$ (10)



Around 500°C,



The second reaction is based on the observation that after 400°C, the amount of cupric oxide is increased to a great extent with the increase of cupric chromite as seen from equation (15).

At about 600°C, cupric chromite and free cupric oxide combine to form cuprous chromite, this conversion being complete at about 1000°C.



In addition to the products mentioned above, there may be some other products in both the cases which could not be identified and which occur in traces even upto 900°C, as revealed by the presence of some very weak lines in the x-ray diffraction pattern.

Crystallographic Properties: It has been mentioned earlier that there is a different opinion about the crystal structure of cupric chromite. Selwood *et al*³ reported that the product obtained by high temperature ignition of 1:1 mechanical mixture of CuO and Cr₂O₃ possesses spinel structure. Stroupe¹ reported that Selwood's product was a mixture of free chromium oxide and cuprous chromite but not cupric chromite, the latter does not possess spinel structure. A study of the powder pattern in this work supports Stroupe's view on the crystal structure of cupric chromite.

The interplanar spacing and the corresponding Q values ($Q_{hkl} = 1/d^2_{hkl}$) are listed in Table 6. Attempts

were made to index the powder lines with cubic, hexagonal and monoclinic systems and the data did not fit with any one of these system. In such a case the powder pattern was indexed by the analytical procedure. The direct cell dimensions are as follows: $a=4.800 \text{ \AA}$ $\alpha=90^\circ$, $b=3.895 \text{ \AA}$ $\beta=90^\circ$ and $c=3.006 \text{ \AA}$ $\gamma=90^\circ$. The crystal, therefore, belongs to the orthorhombic system. The probable space group is P22 or Pmm2 or Pmmm. Copper hydroxy ammonium chromate ($\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$).

The interplanar spacing and corresponding $\text{Sin}^2\theta$ values are listed in Table 7.

Proceeding in the same manner, the direct cell dimensions were evaluated from the interplanar spacing listed in Table 7. The values are as follows:

$$\begin{aligned} a &= 7.143 \text{ \AA} \quad \alpha = 90^\circ \\ c &= 5.880 \text{ \AA} \quad \beta = 90^\circ \\ \gamma &= 90^\circ \end{aligned}$$

The crystal, therefore, belongs to the tetragonal system. The probable space groups are P4/m, P4, P422, P4mm, P42m, P4m2 and P4/mmm.

TABLE 6—INDEXING OF THE REFLECTIONS OF CUPRIC CHROMITE (CuCr_2O_4)

dÅ	I/I ₁	Q observed	Q calculated	hkl
4.77	mw	.0439	.0434	100
3.88	w	.0664	.0659	010
3.00	w	.1111	.1107	001/110
2.55	s	.1538	.1541	101
2.40	ms	.1736	.1756	200/011
2.128	w	.2208	.2205	111
1.949	vw	.2633	.2656	020
1.710	vw	.3420	.3502	211
1.633	ms	.3750	.3743	021
1.592	vvw	.3946	.3951	300
1.503	m	.4427	.4444	002/220/310
1.442	ms	.4809	.4813	301/102
1.299	vvw	.5926	.5981	030
1.274	m	.6161	.6164	202
1.252	vvw	.6380	.6365	130/320
1.192	vvw	.7038	.7038	031/022/400
1.108	vw	.8145	.8051	401/302
1.067	vw	.8784	.8774	231/312/222/411
0.9803	vvw	1.0408	1.0397	103/032
0.9550	vvw	1.0965	1.0978	140/113/331
0.9380	vvw	1.1366	1.1372	402
0.8910	vw	1.2596	1.2599	023
0.8550	vw	1.3679	1.3669	303

TABLE 7—INDEXING OF THE REFLECTIONS OF THE INTERMEDIATE $\text{Cu}(\text{OH})\text{NH}_4\text{CrO}_4$

dÅ	I/I ₁	$\text{Sin}^2\theta$ observed	$\text{Sin}^2\theta$ calculated	hkl
7.15	s	.0112	0.112	100
4.97	vw	.0239	.0224	110
3.69	ms	.0437	.0448	200
3.28	s	.0550	.0560	210
2.945	m	.0682	.0672	002
2.737	ms	.0794	.0784	102
2.622	m	.0864		
2.542	ms	.0918	.0896	220/112
2.490	vvw	.0959	.1008	300
2.365	vvw	.1062	.1064	221
2.305	m	.1117	.1120	310/202
2.200	vvw	.1228	.1232	122
1.958	w (Br)	.1544	.1568	222/003
1.848	w	.1740	.1736	113/302
1.832	vw	.1768	.1792	400/312/132
1.774	w	.1890	.1904	410
1.645	vw	.2196	.2184	331/322
1.545	w (Br)	.2490	.2464	402/303
1.483	w (Br)	.2699	.2688	332/004
1.456	vvw	.2801	.2800	500/340/104
1.383	vw	.3108	.3136	204/151
1.315	vvw	.3434	.3416	143/502/251
1.285	vvw	.3597	.3584	440/152/224
1.143	vvw	.4547	.4592	540/144

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Measurement and control of liquid concentration with a high accuracy have been discussed by a newly developed method based on the combined effect of absorption and backscattering of β -particles from $\text{Sr}^{90}\text{-Y}^{90}$ source. The resolving power of the process has been shown to be much higher than that of the earlier methods utilizing either absorption or backscattering of β -particles separately. Measurement of concentration of some ammonia compounds used as fertilizer has also been discussed and a calibration curve has been given for the quick and efficient determination of percentage composition of ammonium sulphate and ammonium nitrate in the double salt.

Beta-Backscattering and Absorption Combined Method for Measurement and Control Of Liquid Concentration

By S. K. DAS AND K. N. PAL,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Automatic control and measurement of liquid concentration is of great importance in chemical industry. Several methods are in vogue for the measurement and control of liquid concentration. Radio-isotopes have also been used for the same purpose which utilize either the backscattering¹ or absorption² of β -particles. The mathematical basis for the construction of gauges for that purpose have been discussed in detail in the previous publication³.

The intensity of β -backscattering from a medium of infinite thickness depends mainly on the atomic number of the scatterer. However, for very light elements the orbital electron contribution cannot be totally neglected. The dependance of the β -backscattering process being thus very sensitive to the atomic number of the scatterer, high atomic ions may easily be detected in a medium of low atomic number by this process. Therefore, measurement and control of concentration of water solution of any salt possessing higher atomic number than that of water may be done by utilizing backscattering. However, backscattered β -radiations from such water solutions consist of two components, viz. (a) soft component due to water, and (b) a hard component due to its salt content, the former being of much less intensity in comparison to the latter and thus can easily be cut out by suitable absorber. The amount of the measured harder component of the backscattered radiation is, therefore,

proportional to the salt concentration. It may also be mentioned that for a constant thickness of water solution of any salt, absorption of β particles through it will also be proportional to its concentration.

In the present investigation, measurement and control of water solution of different salts covering a wide range in the periodic table, such as acetates of lead ($Z=82$), barium ($Z=56$) and zinc ($Z=30$), have been studied by a newly developed method based on the combined effect of absorption and backscattering of β -particles from a $\text{Sr}^{90}\text{-Y}^{90}$ source. A comparison of results obtained by this method with those obtained by the earlier methods utilizing β -absorption or backscattering separately (Table 1) shows that the resolving power of the developed process is much higher. Moreover, the concentrations of some solutions of ammonia fertilizers have also been measured and a calibration curve has drawn for a quick and efficient determination of percentage composition of ammonium sulphate and ammonium nitrate in the double salt.

Experimental

The essential features of the experimental set up are shown in Figs. 1 & 2. Two organic quenched G. M. tubes of window thickness 1.5 mg./cm^2 and diam. 3 cm. were used in conjunction with two linear count-rate meters capable of counting upto 10^4 counts/sec. with an

TABLE 1—RELATIVE RATIO OF RESOLVING POWERS OF THE THREE METHODS AT DIFFERENT CONCENTRATIONS

Measuring Liquid (At 27°C)	Concentration, g./100 cc	Relative Ratio of Resolving Powers		
		By Absorption Method	By Back-scattering Method	By Back-scattering and Absorption Combined Method
Lead Acetate	10±2	12.0	11.75	23.25
	20±2	10.25	9.25	19.00
	30±2	9.25	7.50	15.75
Barium Acetate	10±2	9.0	8.5	16.75
	20±2	8.0	7.5	14.75
	30±2	7.5	7.0	14.00
Zinc Acetate	10±2	4.5	2.5	6.75
	20±2	4.5	2.5	6.75
	30±2	4.5	2.5	6.75

integral time-constant variable from 0.5 to 85 sec.

Two Sr^{90} — Y^{90} sources, each of one millicurie strength, were used as β -emitters. For absorption studies the source was deposited and sealed by a thin sheet of stainless steel inside a drilled hole of 1 mm. diam. and 5 mm. deep at the end of a stainless steel rod of diam. 5 mm. and length 14 cm. For backscattering, the source was kept inside a narrow hole of 5 mm. depth at the centre of a small lead bead embedded inside a perspex sheet which also supported the G.M. tube for detection of backscattered β -particles. The spatial relationship between the absorption and the backscattering sources and the corresponding G. M. tubes were kept fixed at the best feasible geometry⁴ and proper shielding was provided so that each of the G. M. tubes could detect the individual effect only.

The sources and the G. M. tubes were arranged in a perspex cell (Fig. 1), which consisted mainly of two compartments. The upper chamber was essentially a liquid container of capacity 160 c.c. with two mica windows at its base, one of which was circular of 3 cm. diam. and was placed over the absorption detecting tube (G. M. tube 1) and the rest was elliptical covering the source top and the tube detecting the backscattered radiations (G. M. tube 2). Inlet and outlet connections were provided with stopcocks to allow continuous flow of liquid inside the chamber, when necessary. The outflow tube was also used for the maintenance of a constant liquid level during measurements, which was necessary for exertion of a constant pressure over the mica windows. The height of the liquid level was so chosen that it was

more than the saturation thickness of the measuring liquid. The rod with absorption source was kept immersed inside the liquid at the centre of G. M. tube 1 (Fig. 1), through a slot in a perspex stand mounted

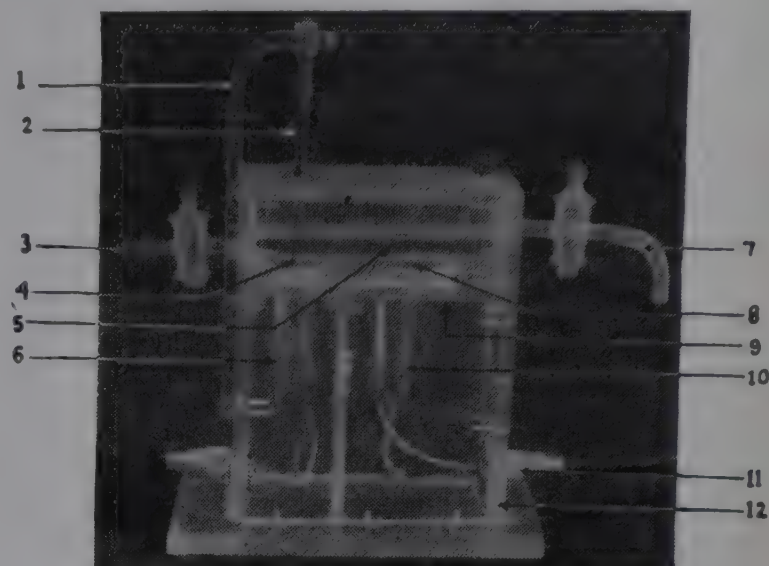


Fig. 1—Liquid Cell with G.M. tubes and source assembly

1. Absorption Source Stand; 2. Absorption Source Rod; 3. Liquid Inlet; 4. Mica window (absorption); 5. Measuring Liquid; 6. G. M. tube—1 (absorption); 7. Liquid Outlet; 8. Mica window (Backscattering); 9. Source for BS; 10. G. M. tube—2 (BS); 11. Receptacle of UHF—Connector; 12. Perspex Container.

with the assembly. The supporting end of the source rod was threaded and two nuts provided the facilities for fixing and adjusting its height inside the liquid. The lower compartment of the cell consisted of two chambers separated by thick perspex sheet, one containing the absorption measuring and the other backscattering measuring G. M. tube, the leads of which were connected to receptacles of U.H.F. connectors fixed on the cell wall.

The circuit assembly for the measurement of G. M. pulses (Fig. 2) was similar to that described earlier³. G. M. tubes for detection of absorption and backscattering were connected to the linear count-rate meters mentioned earlier. Besides the meters C_1 and C_2 , which measured the individual count-rates, the output of the

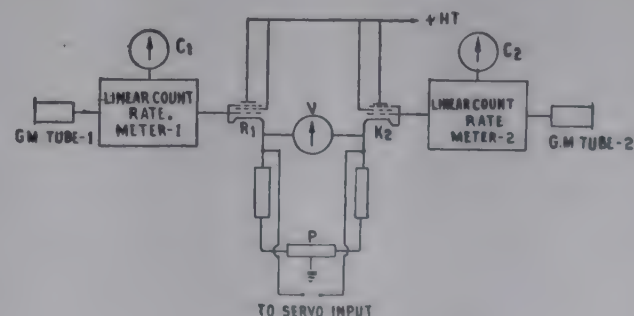


Fig. 2—Block Circuit Diagram

linear count-rate meters was fed through the cathode followers K_1 and K_2 to a voltmeter V of suitable range and sensitivity. The latter would therefore, record the voltage difference developed across the cathode followers and its readings could be set to a desired value by means of a potentiometer (P). Evidently, the voltage developed across the cathode followers would be proportional to the counts obtained by the G. M. tubes.

With the increase or decrease of the concentration of measuring liquid the absorption count would necessarily be decreased or increased. The reverse would be the case for the backscattering effect. But the voltmeter would get the addition effect of the small change of opposite voltages across the cathode followers connected to absorption and backscattering assembly separately and would produce a relatively large deflection as described earlier³. The voltage plotted graphically against different known concentrations of the measuring liquids would give the calibration curves which could be used for the measurement of unknown concentrations. The scale of the voltmeter, therefore, might be converted to concentration after proper calibration. The experimental arrangement for the controlling of liquid concentrations has been discussed later.

Results and Discussion

For the measurement of liquid concentration, calibration curves were first plotted between the count-rate and the known concentration of the measuring liquid upto saturation. All measurements were taken at 27°C.

Fig. 3 shows the absorption curves for acetates of lead, barium and zinc as measured by the count-rate meter C_1 . The backscattering curves for the same compounds measured by the count-rate meter C_2 are given in Fig. 4. In the absorption and backscattering

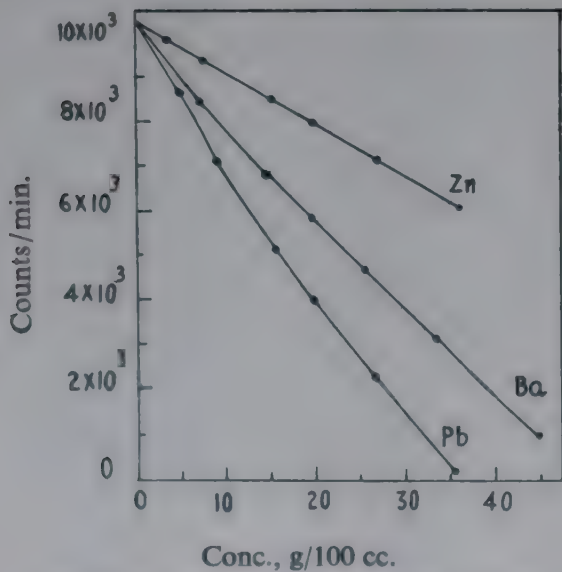


Fig. 3—Absorption Curves for Pb, Ba and Zn Acetates

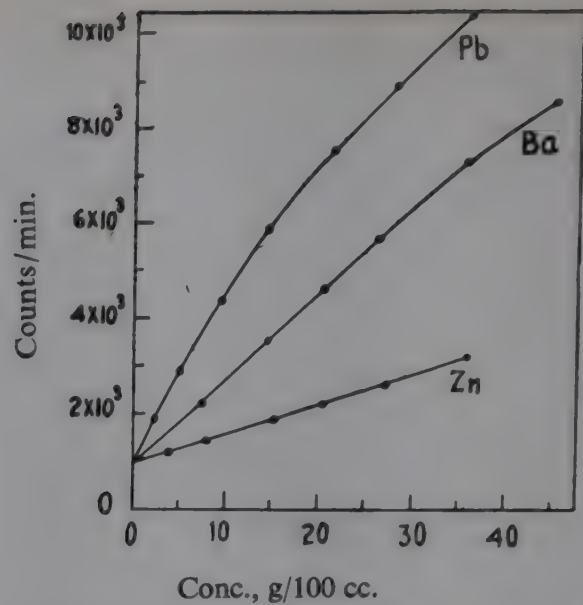


Fig. 4—Backscattering Curves for Pb, Ba and Zn Acetates

combined process, count-rates were noted simultaneously from the meters C_1 and C_2 and the corresponding voltage difference across cathode followers K_1 and K_2 was also recorded by the voltmeter V for each known concentration of the measuring liquid. The curves thus obtained (Fig. 3) are used for calibration for the present process. Though the readings from the voltmeter were sufficient for calibration, readings from C_1 and C_2 were also taken just to compare the efficiency of the present method with those processes utilizing only absorption or backscattering of β -particles individually.

The compounds of lead, barium and zinc were chosen for the present study because their atomic numbers (Z) are different and in the decreasing order, viz. 82, 56 and 30 respectively. Since the acetates of lead, barium and zinc were used, the variation in the nature of absorption or backscattering curves were evidently due to the difference in atomic numbers (Z) only.

The advantages of the present method with the combination of absorption and backscattering of β -particles over the earlier methods using each of them individually can be best understood by comparing the resolving powers of the above three methods. The resolving power (R. P.) may be defined as the ratio of the output variation (dI) to the variation of the quantity to be measured (dC), i.e., $R. P. = dI/dC$. Here, dI represents the change in the β -flux measured by the counters corresponding to the change in the concentration dC of the measuring liquid. An actual comparison of the resolving powers of the three methods obtained from the Figs. 3 to 5 has been shown in Table 1 for different concentration ranges. The results clearly indicate that the resolving power of the present process is much higher in comparison to that by the other methods.

The developed process was also adopted to control

$$Z = \frac{m(A_b Z_b) + n(A_c Z_c)}{\text{mol. wt. of } B_m C_n}$$

where A_b and A_c are the atomic weights of B and C⁶. Therefore, the present method with combined effect of backscattering and absorption is not much useful for compounds with effective Z less than 16. Hence, the concentration of some ammonia compounds whose effective Z were less than 16, such as ammonium sulphate, ammonium nitrate and urea—commonly used as fertilizers—was measured by the absorption process only with the help of a single count-rate meter. Moreover, the effective backscattering of β -particles from hydrogen being negative⁶, that from ammonia compounds will also be necessarily negligible in comparison to the absorption. The result for the aforesaid ammonia fertilizers has been shown in Fig. 6. However, though the absorption of β -particles by such compounds is also less, sufficient accuracy in results has been achieved by proper adjustments of source strength as well as thickness of absorption medium.

The measurement of percentage concentration of ammonium sulphate and ammonium nitrate in the solution of a double salt has also been done with high accuracy and corresponding calibration curve shown in Fig. 7. For this purpose, the solution was taken near the saturation for ammonium sulphate, in which ammonium nitrate was mixed up at different percentages.

The concentration of ammonia fertilizers described above may also be controlled for any desired value by the similar controlling arrangement as discussed earlier. A single count-rate meter should be used instead of two, because only the absorption process is effective for such ammonia compounds.

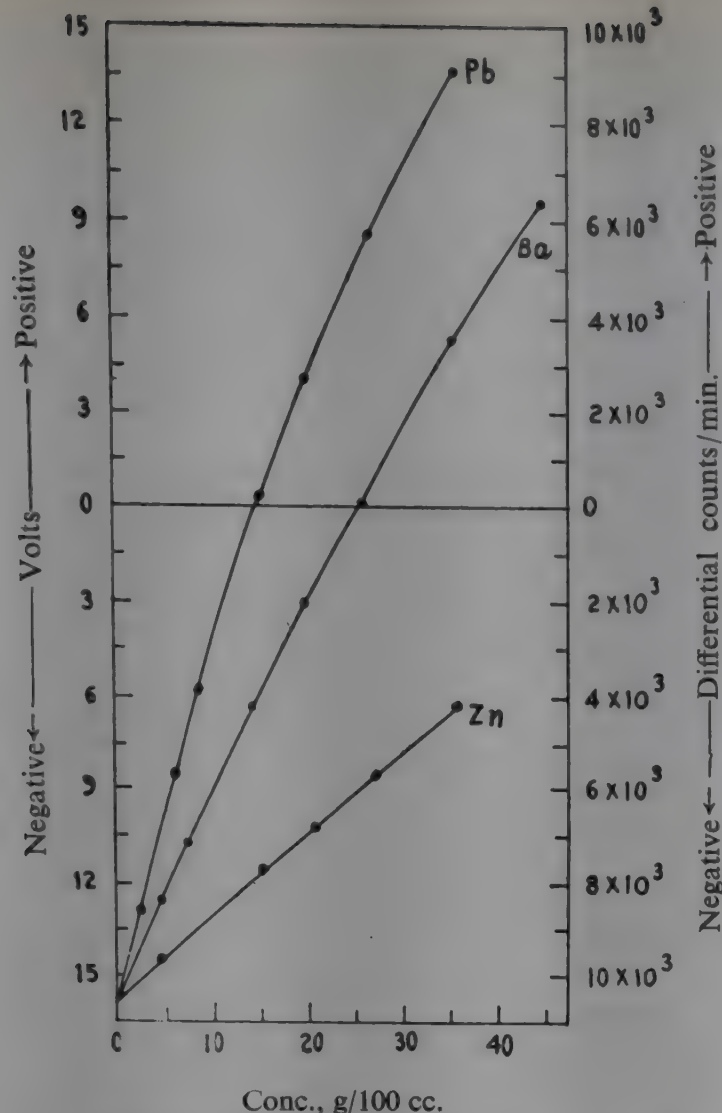


Fig. 5—Backscattering Absorption Combined Curves for Pb, Ba and Zn Acetates

any desired concentration of the liquid using servo-mechanism. The input of the servo-amplifier was connected to the cathode followers K_1 and K_2 and was fed through a servo-amplifier to a servo-motor. For controlling any desired concentration, the deflection in the voltmeter V was first made zero by equalizing the voltages in K_1 and K_2 . This was done by making the count-rates in the rate meters equal by adjusting the intensity of β -particles. The condition was achieved by proper adjustment of the source for absorption purpose, because the source for the backscattering was kept fixed at the best feasible geometry. Any finer adjustment necessary to make deflection of voltmeter V zero was done by the potentiometer P (Fig. 2). In the laboratory, concentration of the measuring liquid was maintained at any desired value by controlling the dilution of a concentrated solution by aforesaid servo-mechanism. Better results were obtained by the present process in comparison to the earlier processes with individual effect of absorption or backscattering.

It has been well established that backscattering of β -particles from compounds with effective Z below 16 is very less⁵. The effective Z of a compound $B_m C_n$ may be defined by the relation:

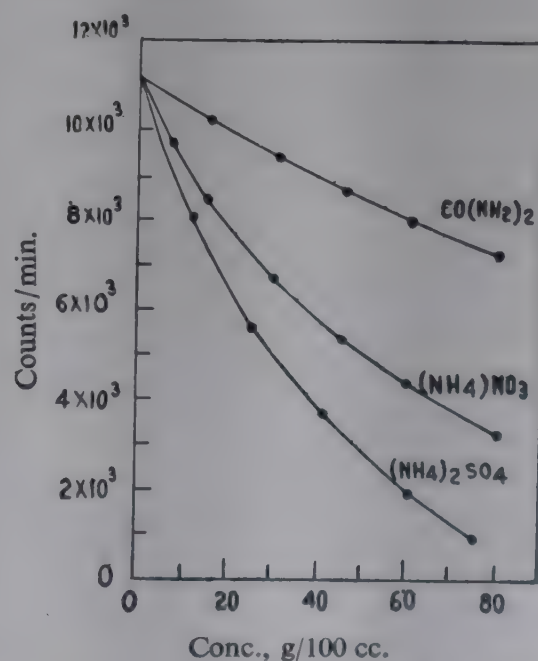


Fig. 6—Absorption Curves for $(NH_4)_2SO_4$, NH_4NO_3 and $CO(NH_2)_2$

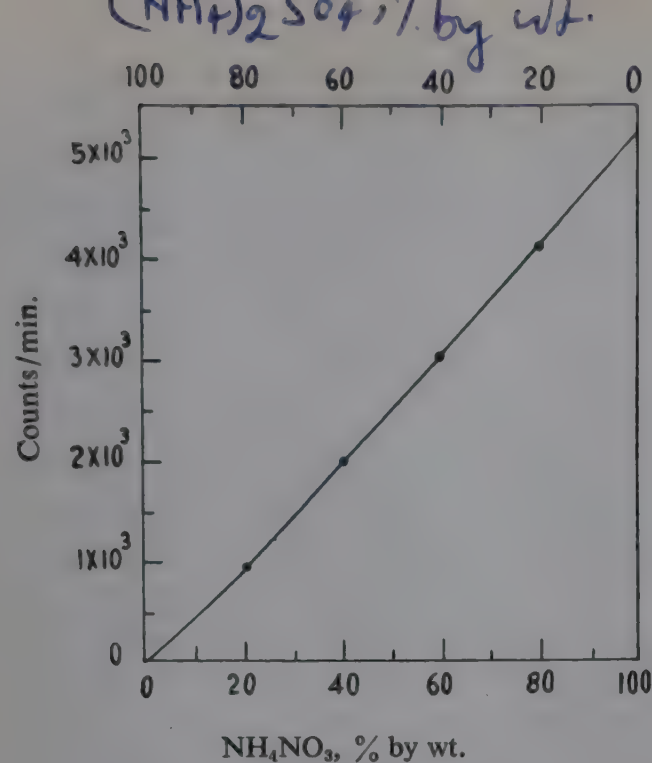


Fig. 7

The percentages of ammonium sulphate and ammonium nitrate in the double salt when used as fertilizer are usually 63 and 37 respectively, which give a total effective nitrogen content of about 26 per cent. The calibration curve for the double salt (Fig. 7) can be utilized for quick determination and control of the percentage of ammonium sulphate and ammonium nitrate in it with a high accuracy.

In all of the experiments discussed so far, G. M. counters have been used as pulse detectors. A still higher accuracy and more precision-controlling, based on the developed method, may be achieved utilizing β -scintillation unit. It may be noted that the two identical rate meters—one for absorption and the rest for backscattering measurement—being connected in opposition acted as compensatory circuits and thus nullified errors due to change in the circuit conditions. However, it is quite evident that as the method is based on the combined effect of absorption and backscattering of β -particles, maximum efficiency will be achieved when the gradients of the absorption and the backscattering

curves from the liquid sample will be almost equal, which could easily be done by the proper adjustment of the absorption source and liquid thickness.

Instead of using two Sr^{90} — Y^{90} β -sources, the process was tried also with a single source. The absorption source in Fig. 1 was removed and the backscattering source was used for both the purposes. The end-window G. M. tube 1 was sealed with a separate thin mica sheet and was kept immersed in the measuring liquid by a suitable stand. For control of liquid concentration, the pulses of β -particles through G. M. tubes 1 and 2 were made almost equal by proper adjustment of the height of the G. M. tube measuring the absorption effect, but the results thus obtained was not very satisfactory. Moreover, on using the single source (backscattering source as mentioned earlier) air bubbles were very often found to stick on the mica window of G. M. tube 1, as its area was large (7 sq.cm.) creating serious error in measurement by decreasing the effective liquid thickness. However, with two β -sources no such trouble was encountered due to the narrow end of the absorption source-rod dipped in the liquid.

Finally, it may be mentioned that Sr^{90} — Y^{90} has been chosen as source because it emits high energy β -particles (0.54 Mev. for Sr^{90} and 2.25 Mev. for the daughter Y^{90}) and has a long half-life period (28 years).

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Some practical circuits of transistorized level switches are described here whose performance has been tested between 0 to 50°C. These can be well applied to the metallic contacts and liquids up to the conductivity of 50 μ mho and used in industry as low and high level alarms, level control, level indicator, etc.

Transistorized Level Switching Circuits (On/Off Controller) and Their Possible Applications To Water Reservoir—II

By G. P. GUPTA,

*Planning & Development Division,
Fertilizer Corporation of India Ltd, Sindri, Bihar*

In modern industries remote control plays an important role in automatic control of processes. This helps in centralizing the control of all process variables into a control room. Electrode-type level switching circuits help to it by monitoring and controlling the level of conducting liquids (though feebly conducting), such as aqueous solutions of acids, bases and salts, water, milk, sugarcane and fruit juice, alcohol, beer, etc. A developing city also needs the monitoring and control of water level in various distant or nearby reservoirs to meet the daily demand of water. The close observation and control over the water reservoirs has become essential when there are considerable fluctuations in the daily consumption of water e.g. on holidays and festivals.

Level switch is an important tool to tackle the liquid level problems. In this paper some of its practical circuits are given. Though its performance has been tested between the ambient temperatures of 0 to 50°C, it may work beyond this range also.

Transistorized (Level Switching Circuits)

The theoretical approach to the design of transistorized level switching circuits has already been discussed in Part I¹. Here only their practical descriptions are given. These circuits with the mentioned transistors can be used approximately up to the conductivity of 50 μ mho but its exact value will depend upon many factors, such as size of the electrode, conductivity of the liquid, proximity of the electrode with the container etc. The approximate values of the resistances which can act as

a switch for each of the circuits are shown in Table 1. The approximate values of β for CIL 532 and CIL 221 at the working condition are 200 and 90 respectively.

The first circuit described here (Fig. 1) is of differential type in which the relay coil-load is placed in the collector circuit of T_2 whose base is maintained at a constant potential through the low value resistors R_1 and R_2 . The electrodes A and B are open, the potential of the emitter of T_2 is negative with respect to its base due to the conduction of T_1 and therefore T_2 is cut-off, relay is in the de-energized condition. If A and B are shorted, current in T_1 decreases and base of T_2 swings towards negative which ultimately cuts off T_1 and hard on to T_2 making the relay, RL_1 to energize. The converse state

TABLE 1

Fig. No.	R_{AB} K. Ohms (approx.)	Energized State with Electrodes A & B Kept	V_{AB} (Open), Volts (approx.)	I_{AB} (Max), μ amp (approx.)
1	0-8	Close	3.5	600
1 (Converse)	0-8	Open	3.5	600
2	0-200	Close	12	50
3	0-200	Open	24	60
4	0-200	Close	2.5	7
5	0-1000	Close	15	35

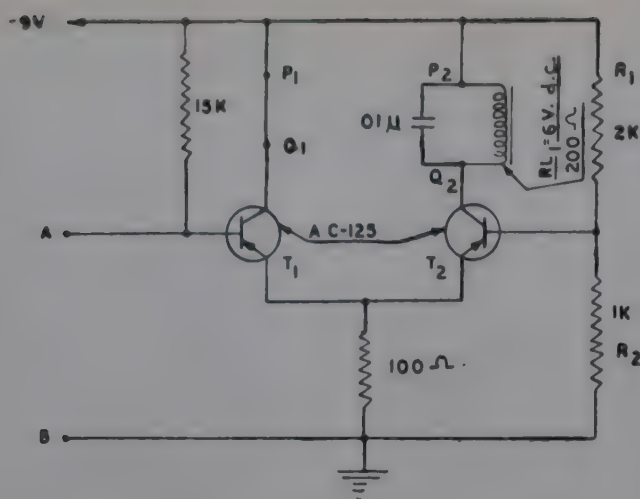


Fig. 1—Close Electrodes (A & B) Energized State

i.e. the energized condition of relay with AB open is obtained if the relay load is placed in the collector circuit of T_1 i.e. relay is connected between P_1 and Q_1 while P_2 and Q_2 are shorted.

This circuit is quite useful for the Annunciator circuit² because a simple alteration in the connections among Q_2 to Q_1 will change the abnormality acceptance point from open contact to close contact type (de-energized condition) and vice versa. This alteration can be made at the spot by interchanging the connections of the jumper placed across $P_1 Q_1$ and the relay tags connected across $P_2 Q_2$ which helps the plant designers to use either open contact or close contact abnormality or both from the same instrument.

In Fig. 2 relay is energized when the electrodes A and B are shorted through R_{AB} i.e. with A and B open, relay is de-energized. Normally transistor T_1 is biased through R_1 which makes it to bottom in turn the base of T_2 , a PNP transistor is more near to the positive end and so T_2 is reverse biased compelling the relay to remain in the de-energized condition. If A and B are shorted through R_{AB} , T_1 is not biased properly making its output impedance to rise and thus R_2 is sufficient to bottom T_2 and relay RL_2 is energized.

This circuit is used as a low-level alarm. The electrode

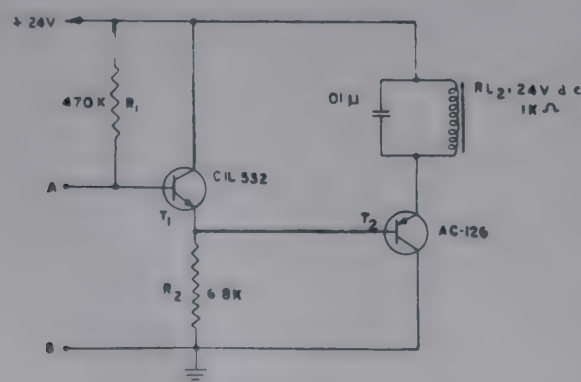


Fig. 2—Close Electrodes Energized State

A is kept immersed in the liquid to a particular depth compelling the relay to remain in the energized condition. As the level falls below the pre-set position of A, relay de-energizes giving an alarm indication.

The function of the circuit shown in Fig. 3 is just the converse of Fig. 2. Here the relay is kept in the energized condition with AB open. Since T_1 is an NPN silicon-transistor and is biased only when A and B are shorted together. If A and B are kept open, T_1 can be considered as open circuit allowing R_1 to bottom T_2 heavily in turn relay RL_3 is energized. If A and B are shorted, T_1 acts as a short-circuit taking the base of T_2 to ground which in turn de-energizes the relay RL_3 .

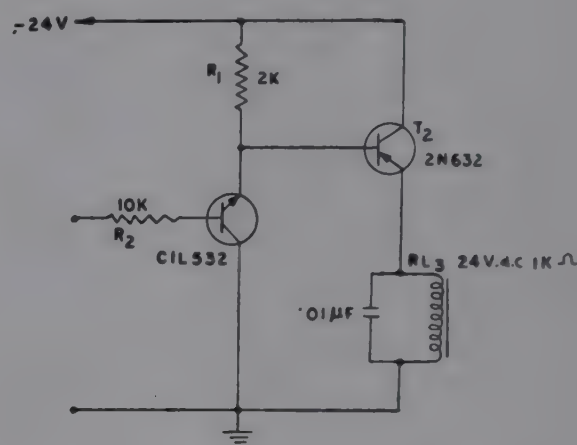


Fig. 3—Open Electrodes Energized State

This circuit has its utility as high level alarm and its action is just similar to that of low level alarm. Here the relay will change its state when liquid level touches the electrode A, positioned at a pre-set height above the liquid level in the container gives an alarm indication.

Normally in a circuit, like low and high level alarms, annunciators, tripping devices, etc., the relay is kept energized and it de-energizes when the pre-set value of the level condition changes. If a relay is kept de-energized in the normal condition then the circuit used for high level alarm will now be applicable to low level alarm and vice versa.

In Fig. 2 an NPN transistor is used for primary switching but if PNP transistor is to be used then circuit of Fig. 4 should be employed. Here T_1 and T_2 are used for primary switching which increases the gain to a quite large value and thus reduces the input current to a maximum value of only 7μ amp. When A and B are open T_2 is bottomed and T_3 is cut off keeping RL_4 in the de-energized condition. Converse action takes place if A and B are shorted together.

The circuit shown in Fig. 5 is also characterized by close electrode energized state but it can be switched

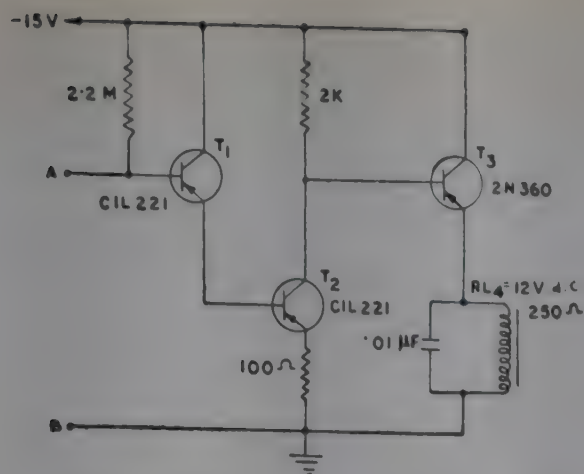


Fig. 4—Close Electrodes Energized State

off for a very high value of R_{AB} utilizing a single transistor as the primary switch.

In Table 1 the necessary switching data of the five circuits so far described are given where R_{AB} represent the range of the resistance for the switching action, V_{AB} the open circuit voltage across AB and I_{AB} the current through R_{AB} .

Applications

Some uses of these circuits have already been mentioned at the time of their individual description. Now some of these circuits will be compiled together to monitor and control the liquid or water level of a number of reservoirs situated at different parts of a city or in an industry.

The complete circuit is shown in Fig. 6 where $R_1, R_2, \dots$ are the reservoirs situated quite distant from each other and connected to the main water line through solenoid valves or pumps as the case may be. All the electrode leads are brought to a central control room where each reservoir has its own control panel and the operator is always kept aware of the water level position from each of the reservoirs.

The complete monitoring circuit (Fig. 6) is divided into three parts—level control, level alarm and level indication. The control circuit consists of two electrodes

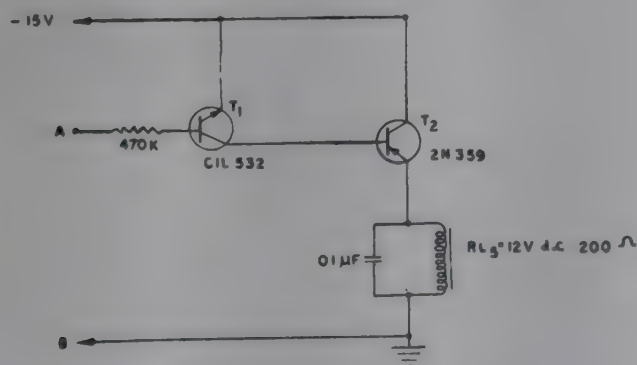
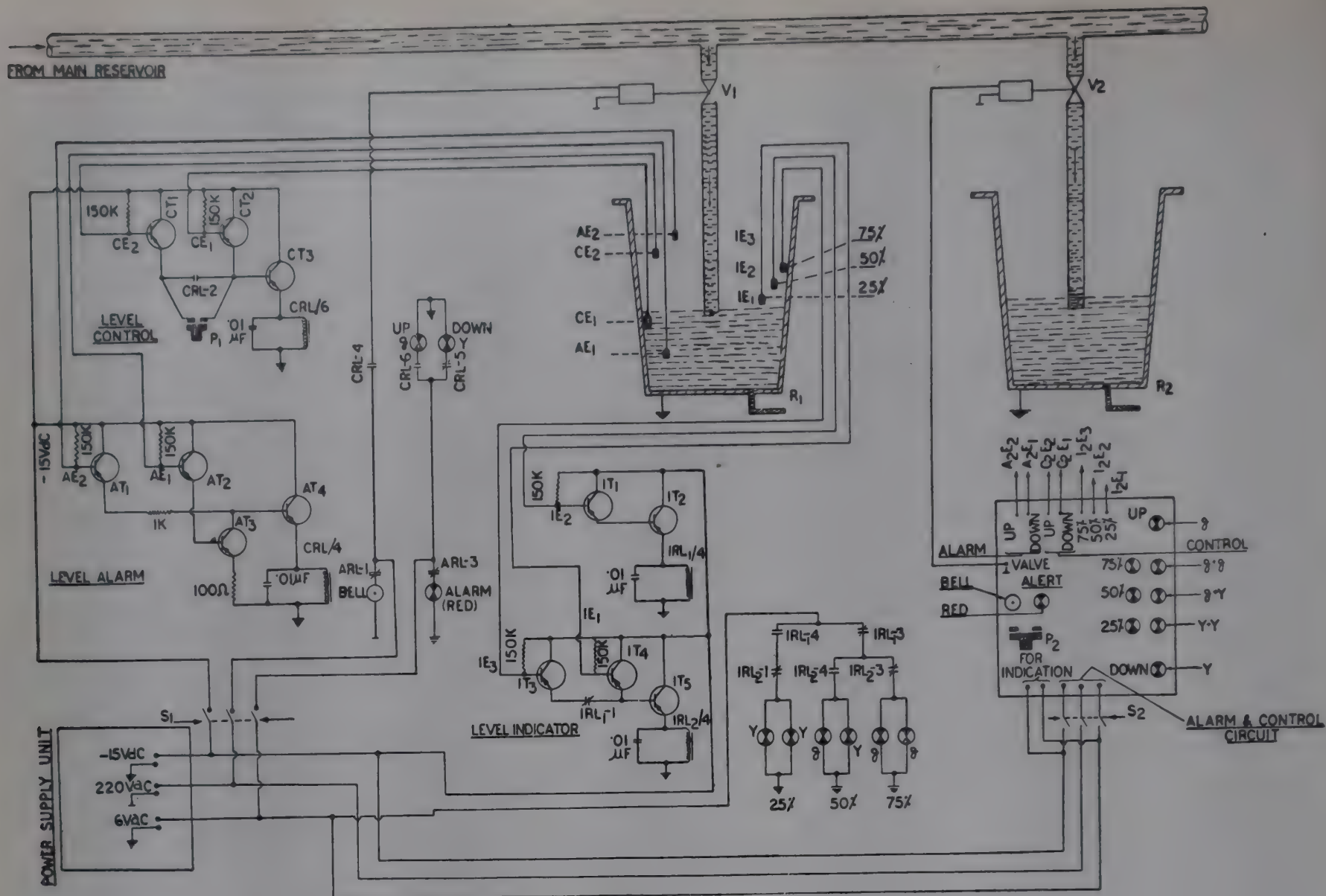


Fig. 5—Close Electrodes Energized State

CE_1 and CE_2 , between which water level is always maintained. Normally, the relay CRL is energized which makes the relay contact CRL-4 close in turn V_1 is open and water rushes to the reservoir R_1 from the main water line. When the water level touches the electrode CE_1 the transistor CT_2 is cut off but CT_3 is on because it is getting the power from CT_1 through CRL-2 and so water is still running into the reservoir R_1 . As the water level touches CE_2 , the transistor CT_1 is also cut off and in turn CT_3 makes the relay CRL to de-energize, thus valve V_1 is closed after filling the tank to a desired pre-set height. Water is continuously consumed, the level falls below CE_2 but the relay still remains in the de-energized condition because CRL-2 is open. If the water level falls below CE_1 the relay is switched on automatically making the valve V_1 open. Thus the function of the control circuit is to maintain the water level between the pre-set electrodes CE_1 and CE_2 and its function is undisturbed and independent from the rate of consumption of water.

The two lamps denoted as up (green) and down (yellow) are used to indicate the operator about the position of the valve whether it is open or close or in other words the water level is going up or down (if the rate of consumption is less than the inflow) respectively. This indication is quite important because the outflow can never be a constant figure throughout the day; it may be maximum at certain periods say at morning and evening and quite low at any other time. If in a reservoir water level is only 25 per cent in the afternoon and if no indication is provided about the position of the valve (open or close) and also a manual control switch then the operator will be in a very embarrassing situation knowing that peak outflow period (evening) is on his head and automatic control will come into effect during that peak period and may remain ineffective because the outflow may be larger than the inflow. Just to avoid such embarrassing situations and to maintain the regular flow of water a separate push button P_1 is provided on the panel. As P_1 is pushed further the relay, CRL is energized making the valve V_1 open and it will automatically be closed as water level reaches the position of CE_2 .

To be sure of the controlling action of the control circuit, an alarm circuit is used whose two electrodes AE_1 and AE_2 are positioned just below CE_1 and above CE_2 respectively to give an alarm indication to the operator about the failure of the control circuit. The alarm indication so received on the empty or overflow side of the tank will be indicated by the glow of the down or up lamp respectively.



NOTE - THE RELAY CONTACTS SHOWN HERE CORRESPOND TO THE DE-ENERGIZED CONDITION OF THE RELAYS

Fig. 6—Circuit Diagram of a Liquid Level Controller, Monitor and Indicator

Normally the relay of the alarm circuit is kept energized within the zone AE_1 and AE_2 , the bell and the red lamp (indicated by alert) both remain off. If water level falls below AE_1 the transistor AT_3 is bottomed through AT_2 making AT_4 open circuit in turn ARL de-energizes giving an audio and visual indication alarm. If the water level just touches AE_2 , the only biasing transistor AT_1 is also cut off, de-energizing the relay, ARL result in an audio and visual indication alarm.

Since in the normal operation the relay is kept energized, failure of d.c. supply will de-energize the relay indicated by an alert signal. Thus, the operation of the automatic control is sure and safe.

The third circuit named as level indicator also plays an important role in monitoring the water level. It consists of three electrodes IE_1 , IE_2 and IE_3 placed at the position of 25, 50 and 75 per cent respectively with respect to CE_1 taken as 0 and CE_2 100 per cent.

Whether the auxiliary control push button P_1 should be used or not will be decided by seeing the water level position indicated by the level indicator.

The relays are normally energized and has no visual indication in this state. As the rising water level touches the electrode IE_1 the relay IRL_2 is de-energized making IRL_2-1 close in turn two yellow lamps glow indicating that water level is above 25 per cent. When the level touches the electrode IE_2 the relay IRL_1 de-energizes making IRL_2 to energize through the contact IRL_1-1 . This time green and yellow lamps are glowing through the contacts IRL_1-3 and IRL_2-4 indicating that level is above 50 per cent. If the level touches IE_3 the relay IRL_2 is again de-energized making the two green lamps to glow through the contacts IRL_1-3 and IRL_2-3 indicating that the level is above 75 per cent.

There is exactly similar monitoring unit for the reservoir R_2 which is shown (Fig. 6) in the form of the

panel only. For indication two lamps in parallel are used to avoid the wrong indication of water level in case of a fused lamp. Separate switches S_1 and S_2 are given for each unit independently to cut off the supply of the control and alarming circuits whenever it is desired to empty the reservoir for cleaning purposes without disturbing the control panel of the other reservoirs.

The monitoring plan (Fig. 6) which has been tested for a model reservoir can be well used for small reservoirs in a laboratory, house etc. or big reservoirs in an industry or city and to show its validity for any level switching problem; it will now be applied to the water system of Sindri town to make the whole system automatic.

Basically all the circuits remain the same to apply them in particular to water system of Sindri town; the only alteration to be made is in the supply connections of the control circuit and the controlling system. Before this alteration is suggested the present water supply system should be followed to have the change with a minimum replacement. The water from a main reservoir, R is driven by a motorized pump into the main line (Fig. 7). The valves V_1 , V_2 , V_3 and V_4 are manually opened and closed which connect the reservoirs R_1 , R_2 , R_3 and R_4 respectively to main line situated at different parts of the town. Now these manually operated valves should be replaced by mains operated solenoid valves (Fig. 7).

The following change should be made in the control circuit to cope with the present problem. A 4-pole C/O relay is used—which is easily available in the market—for each control circuit; connections to the lamps marked up and down are dismantled and separate

switches are used for each control circuit. The complete outside wiring diagram is shown in Fig. 7 which will enable to understand the automatic control of all the reservoirs. To start the automatic control the switches S_1 , S_2 , S_3 , S_4 and so on are switched on. Assuming that there is no water in the auxiliary reservoirs, the switching on of S_1 will close the relay contacts C_1RL-4 and C_1RL-6 in turn valve V_1 is open, pump gets power through auxiliary relay unit and forces the water to fill the tank R_1 while C_1RL-7 is open which cuts off the d.c. supply of the subsequent control units i.e. till the time R_1 is filled up to C_1E_2 (Fig. 6) the other valves remain close. As the reservoir R_1 is full to the mark the relay-contact C_1RL-7 is closed in turn V_1 is closed and control unit for R_2 gets power making C_2RL-4 and C_2RL-6 close. Thus valve V_2 is open and the pump is still getting power through C_2RL-6 . Since C_2RL-7 is now open the other valves are still close. When R_2 is full up to C_2E_2 , V_2 is closed and V_3 open, like this all the reservoirs will be filled up to the mark in the order they are connected. As the last reservoir, R_4 is full, C_4RL-4 and C_4RL-6 are open in turn, pump is closed automatically along with the last valve V_4 and there is no danger of pressurising the main pipe line.

The intermediate situations regarding the position of the water level in different reservoirs can be well controlled by an operator sitting in the control room. Say, for example the area where R_2 is situated consuming maximum amount of water and as the level falls below C_2E_1 the control circuit of R_2 is triggered automatically, result in opening of V_2 and running of the pump to replenish it quickly. If R_2 and R_3 both are discharging

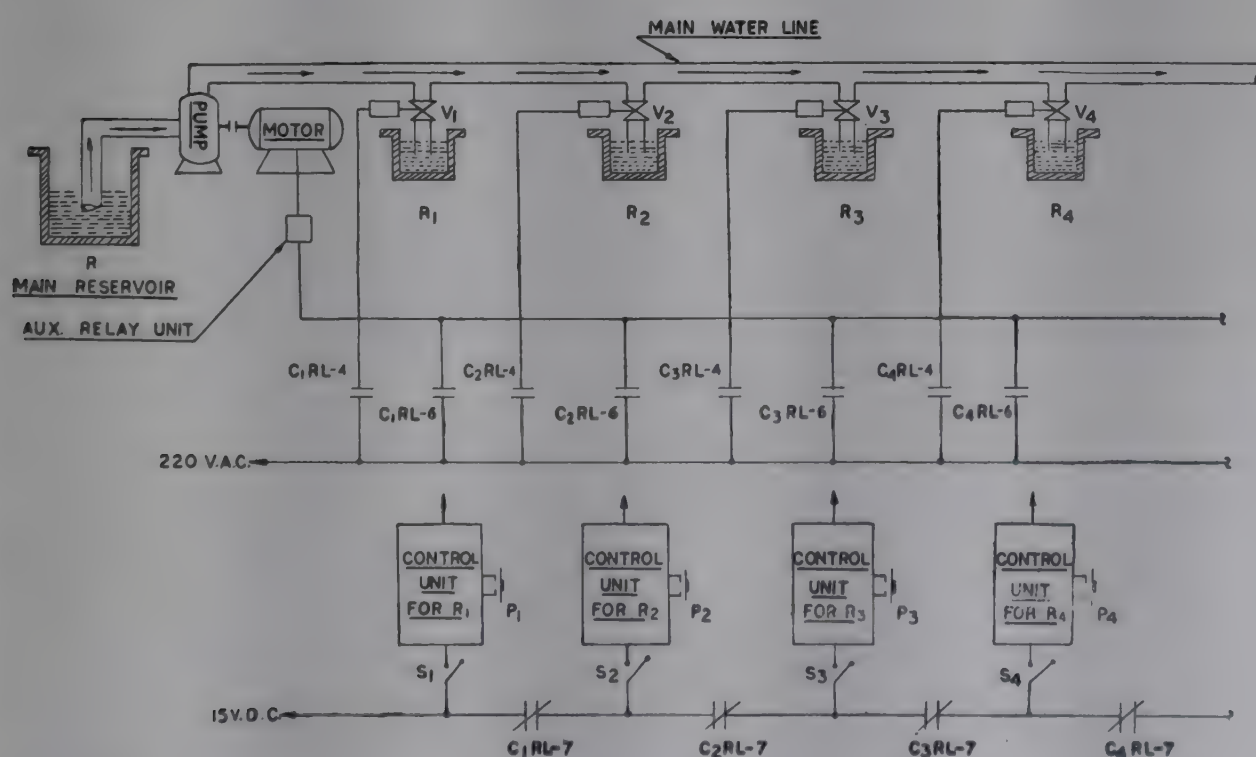


Fig. 7—Automatic Control of Water Reservoirs of Sindri Town (Note: Relay Contacts Shown here Correspond to the De-energized Condition of Relays)

almost with the same rate but rapidly compared to others and it is a fact that if V_2 is open V_3 can not be open and therefore the area where R_3 is situated is in vacuum for water till R_2 is full and just to avoid such oncoming embarrassing situations for the operator which can be well observed from the level indicator, a push button P_3 for the reservoir R_3 , has been provided, pushing of that will energize the relay C_3RL making V_3 open and pump gets on to replenish R_3 quickly. In mean time if water level in R_2 goes below C_2E_1 , automatically V_2 is open and V_3 is closed. Thus water in all the reservoirs can be restored to more normal levels and the supply system can be made more simple, regular and smooth.

If 18 S.W.G. aluminium wire cable is used for connection the resistance for a length of one kilometre is only 22 ohms and it does not affect the controlling system at all even though the reservoirs are several KM away from the control room. But it will certainly affect the power line given to the solenoid valves. Therefore for distant reservoirs an auxiliary relay should be used for each reservoir between the valve and the control circuit.

If it is desirable to use a level alarm in which the relay is kept energized within the zone E_1 and E_2 , the circuit of Fig. 8 should be used. It is self explanatory that if level falls below E_1 or touches E_2 the relay energizes through the transistors T_1 and T_2 respectively.

A close observation on the main water storage tank is necessary and for this purpose a level indicator with a step of 10 per cent indication is described here. If necessary same can also be used for the auxiliary reservoirs. The basic circuit is same but with the help of relay points only five relays are used to control switching of eleven electrodes. The complete circuit is shown in Fig. 9 where lamps are used to illuminate a name plate marked as 'Empty' or 'zero level' or 10 or 100 per cent as the case may be. The function of the circuit is as follows:

Initially when the tank is empty all the relays are energized, the lamp L_1 is illuminating the 'Empty' name

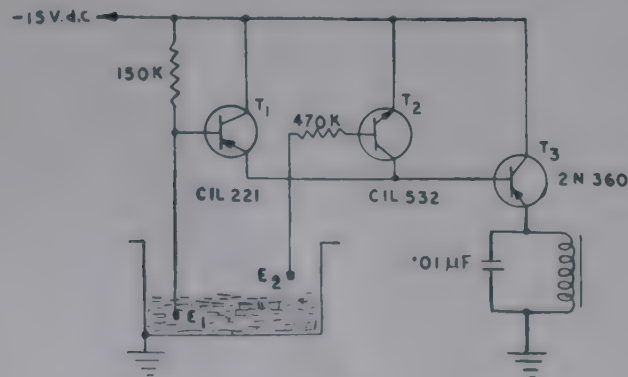


Fig. 8—Level Alarm De-energized within the Zone E_1 & E_2

plate. The lamp L_1 is getting power through the contacts RL_1-1 on one side and RL_2-1 , RL_3-1 , RL_4-1 and RL_5-1 on the other side. If the level touches the zero-level electrode, the relay RL_1 is de-energized closing the contact RL_1-2 in turn the lamp L_2 enlightens the 'zero-level' name plate. This state of relays is shown in position No. 2 (Table 2). When the level touches the electrode E_1 , RL_2 is de-energized making RL_1 to energize through RL_2-7 , L_3 illuminates the plate denoted as 10 per cent which is shown in position 3. If the electrode E_2 is also dipped in water RL_1 is again de-energized making L_4 to get power through contacts RL_1-2 RL_1-6 , RL_2-2 RL_3-1 , RL_4-1 and RL_5-1 which in turn enlightens the name plate of 20 per cent. Like this, energizing and de-energizing of relays continue upto the last electrode and each time a new state of relays is obtained (Table 2) which in turn enlightens a particular name plate indicating the position of the level.

TABLE 2

E=ENERGIZE, D=DE-ENERGIZE

Position No.	State of Relays					Active Electrodes	Name Plate Lights Up
	RL_1	RL_2	RL_3	RL_4	RL_5		
1.	E	E	E	E	E	Nil	Empty
2.	D	E	E	E	E	E_0	Zero level
3.	E	D	E	E	E	E_1	10%
4.	D	D	E	E	E	E_2	20%
5.	E	E	D	E	E	E_3	30%
6.	D	E	D	E	E	E_4	40%
7.	D	D	D	E	E	E_5	50%
8.	D	E	E	D	E	E_6	60%
9.	D	D	E	D	E	E_7	70%
10.	D	D	D	D	E	E_8	80%
11.	D	D	D	E	D	E_9	90%
12.	D	D	D	D	D	E_{10}	100%

The state of relays shown in Table 2 will help to understand the complete switching function of the circuit. If the level is falling down say, it leaves the electrode E_{10} the relay RL_4 is energized through RL_5-3 because RL_5 is still in the de-energized condition making L_{11} (90 per cent level) to glow through the contact RL_4-3 while the lamp L_{12} goes off. As the level leaves the electrode E_9 , RL_5 is energized making RL_4 to de-energize in turn the lamp L_{10} (80 per cent) is illuminated through the contacts RL_3-4 , RL_4-2 and RL_5-1 . Thus this reverse process of switching is also in synchronisation with the fall of the water level and gives an accurate indication of the level with a step of 10 per cent.

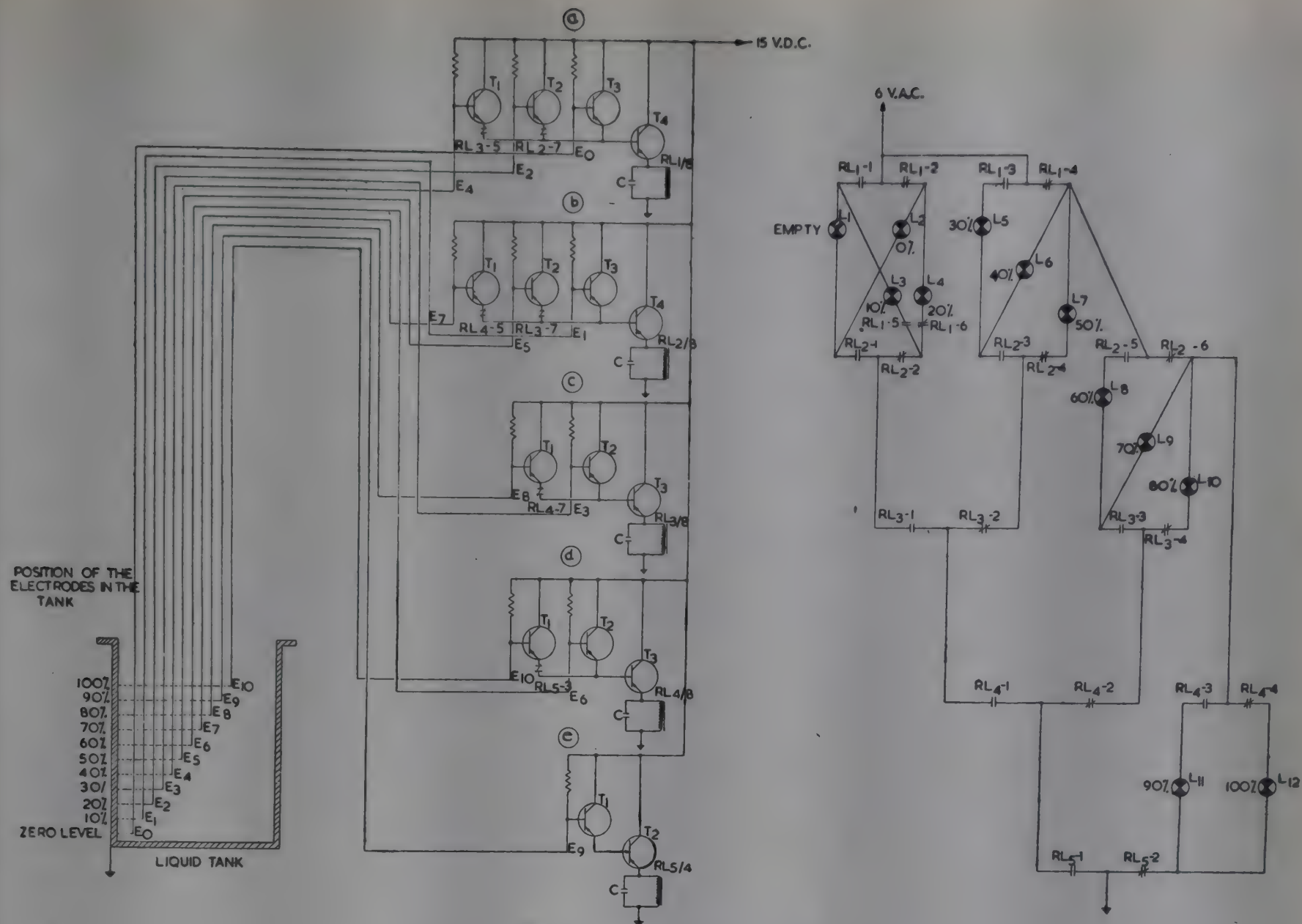


Fig. 9—Level Indicator with a Step of 10 per cent

The level switching circuits so described are quite competent enough to solve many liquid level problems and with proper selection of the transistors and minor change in the circuitry these can be used for de-mineralized water of conductivity $0.5 \mu \text{ mho}$ also.

Acknowledgements

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This paper examines the effect of thermal treatment on the physical parameters of ferric oxide (Fe_2O_3) and ferric oxide-chromic oxide ($\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$) systems. It has been found that a proportionality exists between the average pore radius and grain radius for the reduced as well as unreduced samples. It has also been shown that both particle and pore radii bear a linear relation with surface area.

Influence of Thermal Treatment on the Structural Parameters of Ferric Oxide and Ferric Oxide-Chromic Oxide System

By S. P. SEN, V. K. PURI AND N. C. GANGULI,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

The ferric oxide and ferric oxide-chromic oxide catalyst systems are widely used for the water gas shift reaction. It has been reported in a previous communication¹ that when these systems were heat-treated, the physical structure and texture underwent considerable changes. It has been shown that a linear relationship exists between the conversion efficiency and surface area with the reduced ferric oxide and ferric oxide-chromic oxide samples.

The purpose of this investigation is to find out whether any relationship exists between the particle size and the pore size; and the dependence of surface area on these two parameters.

The physical properties of thermally-treated catalyst samples, viz. A and B series, before and after reduction are shown in Tables 1 and 2. The methods of measurement and evaluation of surface area (S), pore volume (v), average grain ($\bar{r}_g$), and pore size ($\bar{r}_p$) etc. have been outlined elsewhere^{1, -2}.

The ferric oxide catalyst samples A_2 to A_6 and ferric oxide-chromic oxide samples B_2 to B_6 were cured in presence of air at different temperatures for 5 hours. The samples A_1 and B_1 were dried at 110°C for 8 hours. The heat treatment temperatures of the specimens, along with surface area, porosity, particle size and pore size are listed in Tables 1 and 2.

TABLE 1—PHYSICAL PROPERTIES OF THERMALLY TREATED CATALYSTS
(Before Reduction)

Catalyst	Heat treatment, $^\circ\text{C}$	S , m^2/g .	V , cc./g .	Porosity, $\text{cc}/100 \text{ cc}$	$\bar{r}_p$, $\text{\AA}$	$\bar{r}_g$, $\text{\AA}$	$\bar{r}_p/\bar{r}_g$
A_1	110	106.00	0.9373	80.8	177.0	328.0	0.54
A_2	350	40.18	0.9311	81.2	464.0	856.0	0.54
A_3	450	37.58	0.9756	83.4	519.0	942.0	0.55
A_4	600	19.06	0.8945	81.9	939.0	1718.0	0.55
A_5	700	12.54	0.7144	79.0	1139.0	2162.0	0.53
A_6	800	7.80	0.6353	77.1	1629.0	3169.0	0.51
B_1	110	81.00	0.1998	48.6	49.0	152.0	0.32
B_2	350	64.02	0.2225	50.8	69.0	205.0	0.34
B_3	450	37.20	0.2228	51.3	120.0	350.0	0.34
B_4	600	30.35	0.2259	52.7	149.0	424.0	0.35
B_5	700	20.77	0.2360	54.8	227.0	622.0	0.36
B_6	800	13.00	0.2470	58.1	380.0	1014.0	0.37

TABLE 2—PHYSICAL PROPERTIES OF THERMALLY TREATED CATALYSTS

(After Reduction)

Catalyst	Heat treatment, °C	S, m ² /g.	V, cc./g.	Porosity, cc/100 cc	$\bar{r}_p$, Å	$\bar{r}_g$, Å	$\bar{r}_p/\bar{r}_g$
A ₁	110	13.00	1.0076	82.2	1555.0	2827.0	0.55
A ₂	350	12.60	1.0370	83.7	1646.0	2948.0	0.56
A ₃	450	10.00	1.0019	85.5	2004.0	3599.0	0.55
A ₄	600	8.02	0.9327	82.8	2326.0	4211.0	0.55
A ₅	700	6.53	0.9046	83.3	2770.0	5036.0	0.55
A ₆	800	5.00	0.7628	80.1	3051.0	5711.0	0.53
B ₁	110	36.31	0.2345	53.5	129.0	362.0	0.36
B ₂	350	25.88	0.2552	58.0	197.0	526.0	0.37
B ₃	450	23.00	0.2454	55.2	221.0	578.0	0.38
B ₄	600	21.50	0.2409	54.9	224.0	611.0	0.37
B ₅	700	18.04	0.2597	54.6	288.0	759.0	0.38
B ₆	800	10.00	0.2360	54.8	472.0	1290.0	0.36

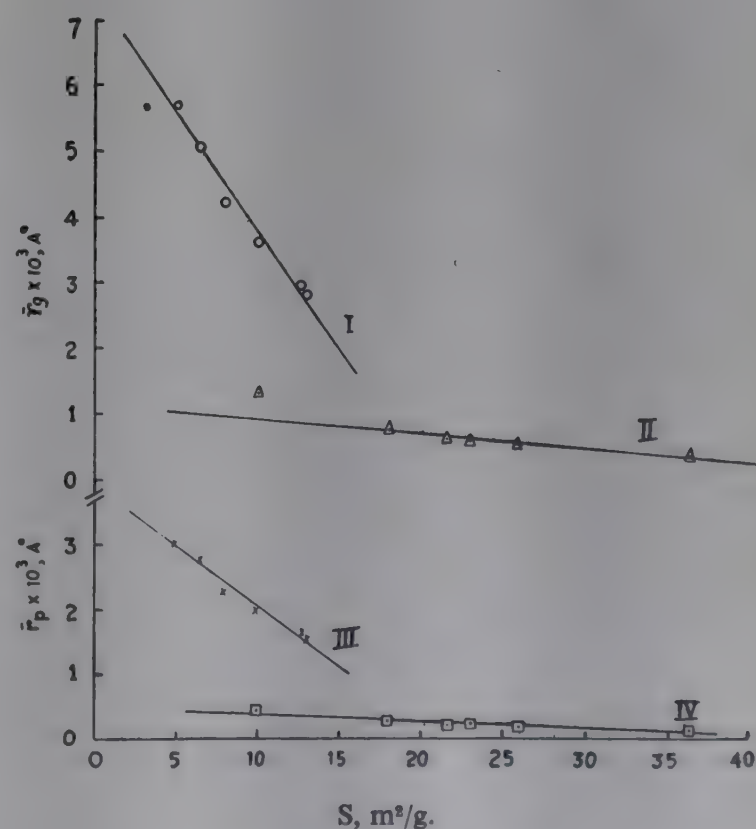
It can be seen (Tables 1 and 2) that a breakdown in the texture of the unreduced ferric oxide system starts from 350°C, and is much pronounced after 450°C which is characterized by the decrease in surface area and increase in particle and pore sizes, whereas, with ferric oxide-chromic oxide system, this is less pronounced. In case of reduced samples, the initial loss of surface area and increase in grain and pore sizes are significant in series A compared to chromium oxide promoted series B.

It has been observed³ that oxides possessing larger surface areas tend to sinter more readily. In the case of the ferric oxide sample, the initial surface area (106 m²/g) dropped to 40.1 m²/g. on heating upto 350°C. Though in the chromic oxide promoted ferric oxide sample the decrease is less pronounced, yet is quite high compared to the successive decreases on further heating beyond 350°C. It can be assumed, according to Ries⁴, that sintering in presence of air occurs by a movement of crypto crystalline material from the surface of wider capillaries to fill the smaller capillaries or pores, so that the average grain size and pore size are increased while the surface area is decreased.

It is clear from (Fig. 1) that with reduced samples, both particle and pore radii bear linear relationship with surface area, whereas in case of un-reduced samples (Fig. 2) this relationship holds good for the ferric oxide-chromic oxide samples only and upto 700°C.

It can be seen (Tables 1 and 2) that the ratios of the

average pore radii to grain radii are rather constant for the un-reduced as well as reduced catalysts. The most striking feature is that though grain and por-

Fig. 1—Plot of Surface Area Against $\bar{r}_g$ and $\bar{r}_p$ of the Reduced Sample

I & III—Fe₂O₃
II & IV—Fe₂O₃—Cr₂O₃

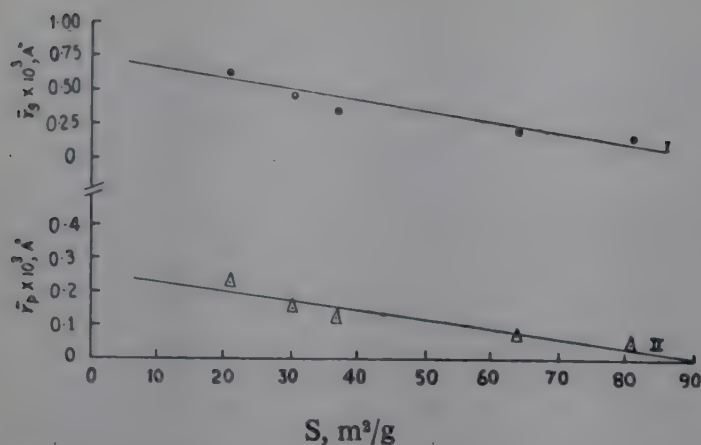


Fig. 2—Plot of Average Grain and Pore Sizes against Surface Area of Unreduced Samples
I & II $\text{Fe}_2\text{O}_3\text{—Cr}_2\text{O}_3$

sizes increase to a great extent on reduction, their ratios are maintained.

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The present authors have already established a strictly linear variation of retention indices of hydrocarbons with column temperatures in all types of stationary liquids. Follow-up research in the present communication reveals a universal validity of the I-T-linearity theory for all types of solute molecules within the whole practical range of temperatures of GLC-liquids. Need for extreme experimental care in obtaining accurate retention data has been pointed out for confirming and utilizing this theory in gas chromatographic identification of peaks.

Versatility of the Linearity of Retention Index with Column Temperature in Gas Chromatography

By G. D. MITRA AND N. C. SAHA,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Saha and Mitra¹ have established a strictly linear variation of Kovats' retention index (I) with column temperature (T) for hydrocarbons in all types of stationary liquids used in gas-liquid chromatography. The objective of this communication is to claim and demonstrate an universal validity of the linear I-T-rule, covering all kinds of volatile solute molecules in partitioning liquids of all polarities in the entire range of the

practical column temperature.

Literature survey reveals conflicting viewpoints regarding the mode of variation of retention index with column temperature. For example, the data of Touress², Evans *et al*³, Widmer⁴, Matukuma⁵, Hively and Hinton⁶ etc. when plotted graphically, give a linear variation of I-versus T. (adamantane type of solutes⁷ in apiezon-L was given in Fig. 1A by way of illustration).

On the contrary experimental results of a large number of workers exhibit very irregular types of I-T plots, one such extreme case^{8,9} was illustrated in Fig. 2A.

Existing mathematical treatments of this problem of I-T correlation do not seem to categorically support a linear variation. Ettree and Billeb¹⁰ have derived a general expression which leads to four possibilities, in three cases retention index becomes invariant with temperature and for the fourth plot of I-versus T should theoretically yield a curve.

Takacs and coworkers⁹ have derived an Antoine-type parabolic relation, which can be approximated by a linear section within a narrow range of column temperature (Fig. 2C).

Under these circumstances, the present authors have undertaken a programme of re-studying literature data as well as experimentally determining retention indices of all types of solutes in various stationary liquids (over their whole practical temperature range) with all possible experimental precautions.

Retention indices of a few representative compounds, namely, toluene, pentanol-2, methyl-2 butanol-1 and n-butylacetate, were determined in neopentyl-glycol-adipate and good linear fits of I-T were obtained (vide Fig. 2B). Same compounds when chromatographed by other workers⁸ on poly-neopentyl glycol sebacate showed very irregular rise and fall of retention index

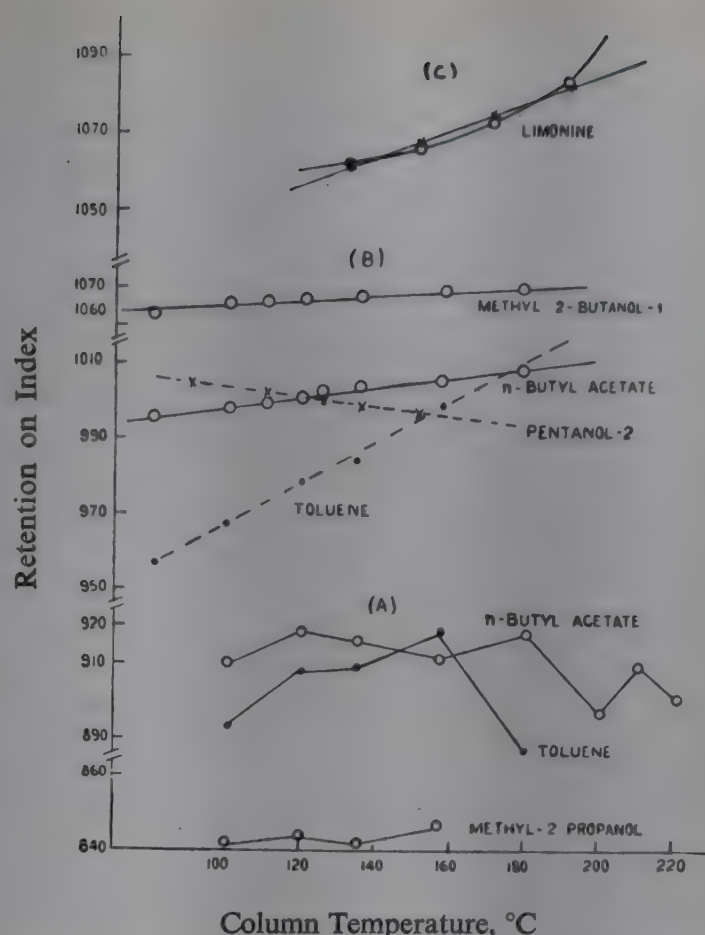


Fig. 2—Variation of Retention Indices of Different Types of Compounds with Column Temperature
(A) Polyneopentyl Glycol Sebacate, REF. (8)
(B) In Neopentyl Glycol Adipate by the Present Authors
(C) In Apiezon n-1 of REF. (9)

with column temperature (Vide Fig. 2A). Limonine in apiezon has been found to give parabolic relation of I-T with one set of literature data, but linear fit with another (vide Fig. 2C).

The present authors obtained excellent linear fit of I-T of polar solutes in a non-polar stationary phase, viz. apiezon-L (vide Fig. 1B). Additional proof with different polarity combinations of solutes and partitioning liquids will be published in detail¹¹. So far, not a single case of non-linearity of I-T in GLC was obtained in this laboratory. It must be emphasised that retention data for the verification of this theory should be determined with extreme care. For example, column operating variables, should be rigidly controlled, supports should not have secondary interaction with solutes, partitioning liquids must be free from impurities and must not undergo any chemical change during use etc.

It is, therefore, highly probable that the linearity of retention index with column temperature is a universal phenomenon in gas chromatography, not at all limited by solute or solvent types or column temperature. We believe that the earlier contrary results in literature, if redone under proper experimental conditions will support this theory.

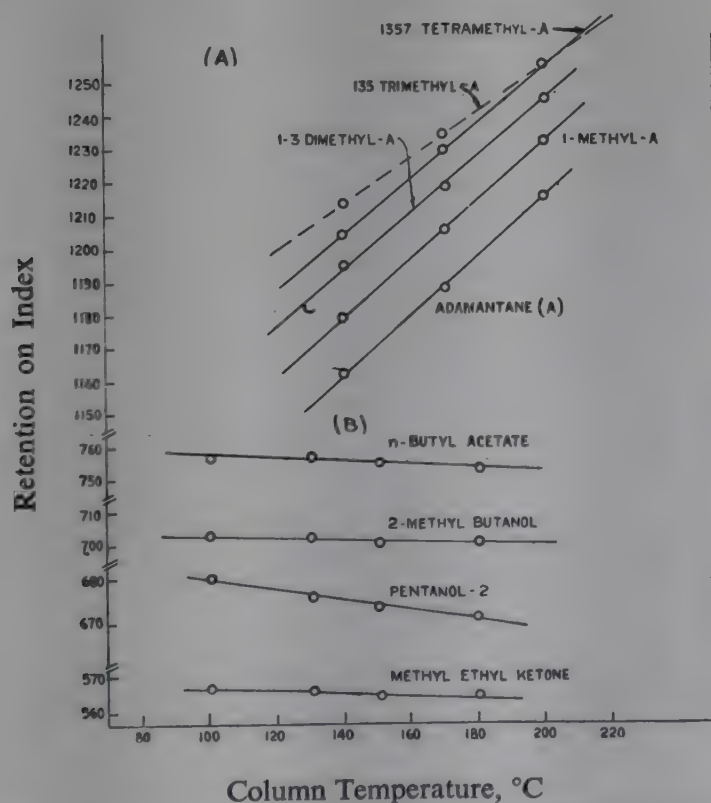


Fig. 1—Variation of Retention Indices of Different Types of Compounds with Column Temperature
A—In Apiezon-1 REF(7)
B—In Apiezon-1

This theory of linear variation of I-T, which can be established by massive experimental data must, obviously, have a solid mathematical foundation. The present authors will deal with this aspect in the detailed report of this work¹².

In conclusion, it can be said that a general acceptance and wide application of this theory will result in one of the most powerful single identification parameters in gas chromatography (probably in other forms of chromatography also) and is likely to give new ideas in the design of next generation of gas chromatographs.

Acknowledgement

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Thermogravimetric techniques have been applied to determine the dehydration characteristics and characterisation of the different types of molecular water present on the surface of the high adsorption capacity, chromatographic grade silica gel, having surface area 811 m²/g and pore diameter 22.9Å, developed in this laboratory.

Thermogravimetric Studies on Surface Water Characteristics of Chromatographic Grade Silica Gel

By A. SINHA AND P. K. MUKHERJEE,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

The process know-how for the preparation of high adsorption capacity, chromatographic grade silica gel, developed in this laboratory and suitable for hydrocarbon types analysis of naphtha and other light distillates of petroleum by Fluorescence Indicator Adsorption (F.I.A.) method of analysis as per A.S.T.M. Standard

D-1319-65T method¹ has been covered by a patent². This gel, having surface area 811 m²/g and average pore diameter 22.9Å, has been used satisfactorily, substituting imported Davison grade 923 gel. Detailed investigations of the physical and chemical properties and characterisation of this gel in terms of least polymerisation activity

and adsorption capacity in binary and ternary mixtures have been carried out³. These investigations have shown that this gel is satisfactory as compared to the imported Davison grade 923 gel and superior to other indigenous gels used for hydrocarbon types analysis by F.I.A. method. The gel possesses high adsorption capacity for aromatics and very little polymerization tendency for olefins.

The surface chemistry and pore geometry of silica gel has been the subject matter of detailed investigations for many years on account of its varied and specific uses. Detailed thermal, chemical, spectroscopic and isotopic investigations have given deep insight into the chemical nature of silica gel surface such as the distribution of Si-OH groups, energy released upon water absorption and characterisation of different kinds of molecular water that may exist on the silica surface. The existence of two kinds of water, physically adsorbed on the silica gel surface and molecularly adsorbed by hydrogen bonding to the silanol groups has been reported by Fripiat *et al*⁴ and Lange⁵.

In view of these observations, the study of the nature and relative distribution of surface water, one corresponding to physical adsorption and the other to the constitution at hydroxyl groups of this high adsorption capacity, chromatographic grade silica gel was considered of interest.

The present communication deals with the study of dehydration characteristics of this gel and characterisation of the different types of molecular water present on the surface of the gel by the application of thermogravimetric techniques. This has a direct bearing on the controlled activation and coverage of the silica gel surface with Si-OH groups for controlling the selectivity in the separation of the components in naphtha by F.I.A. method of analysis.

Experimental, Results and Discussion

Silica gel prepared in our laboratories, mesh size (B.S.S.)—30+60 has been used as such without further purification since the percentage impurity was below 0.11, the silica content being 99.89 per cent on anhydrous basis. The laboratory gel was compared with a commercial gel sample after being exhaustively purified to remove organic matter and then treated with concentrated hydrochloric acid, washed to pH 6.0 and then dried. Table I gives the physical properties of the two samples.

'KeroY' thermobalance has been used to carry out thermogravimetric analysis using tubular silica furnace and temperature programming of 10°C/min. The thermo-

TABLE 1—SURFACE AREA AND ADSORPTION CAPACITY OF SILICA GEL SAMPLES

Sl. No.	Gel Sample	Specific Surface Area (BET), M ² /g	Adsorption Capacity, ml. of toluene (20% soln.)/100 g. gel.
1.	Laboratory gel	811	23.1
2.	Commercial gel	375	13.6

grams of the laboratory and commercial gel are shown in Figs. 1 and 2 respectively. It would be noted that both the thermograms are similar in nature except differing in the water content of different types. The thermograms showed distinct breaks near 120 and at 180°C and a slight break near 140°C indicating the changes in the

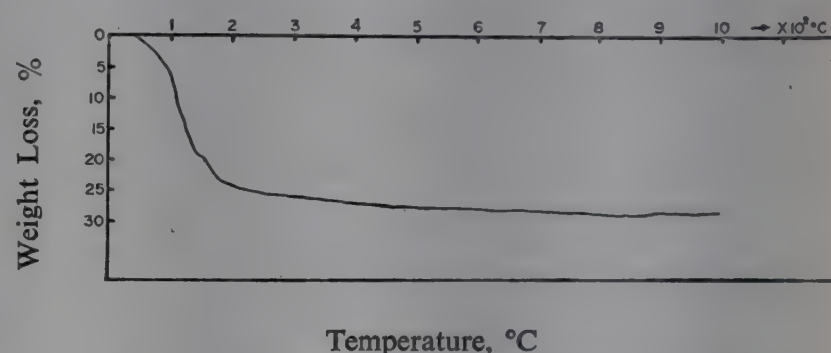


Fig. 1—TGA Thermogram of Laboratory Silica Gel

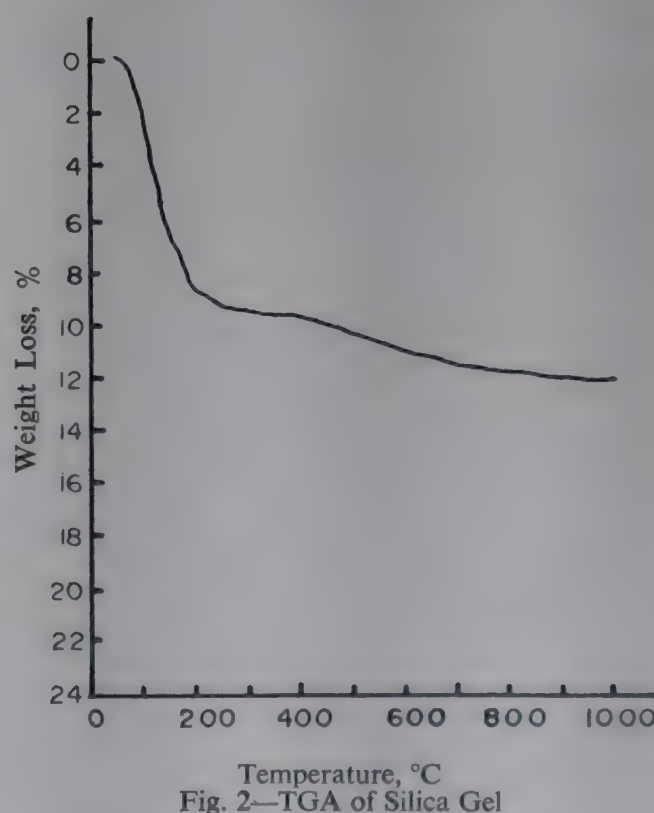


Fig. 2—TGA of Silica Gel

arrangement of water molecules and hydroxyl groups on the surface. It was observed that upto 120°C, the evolution of water was mainly due to water physically adsorbed on the silica gel surface. On raising the temperature above 120°C, the loss in the weight of the sample indicated the evolution of water attached to the Si-OH groups by hydrogen bonding. Table 2 gives in quantitative measure the types of molecular water on the surface of the gel samples.

TABLE 2—TYPE OF MOLECULAR WATER ON THE SURFACE OF GEL SAMPLES

Sl. No.	Gel Sample	Molecular Water, weight %		
		Physically adsorbed (25°-120°C)	H-bonded (120°-180°C)	Silanol derived (180°-500°C)
1.	Laboratory gel	13.55	10.13	3.86
2.	Commercial gel	6.20	2.40	1.60

The curve obtained on plotting dw/dt against temperature of the laboratory gel is shown in Fig. 3. The evolution of water from silica gel surface on heating is an endothermic type of reaction and the temperatures 120 and 180°C are the points at which there is sharp absorption of energy indicating the break-down of the types of water around these temperatures. Physically adsorbed water could thus be differentiated quantitatively from H-bonded water. Young⁶ also confirmed in his observa-

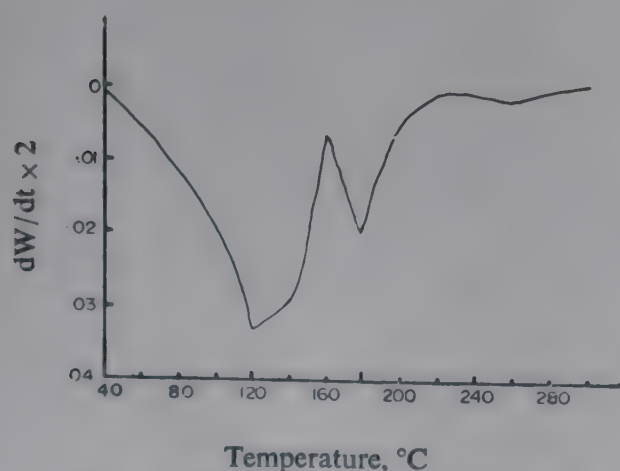


Fig. 3—DTGA of Laboratory Silica Gel

tion that silanol groups are stable upto 180°C. H-bonded water is much more strongly attached to the silanol groups than the physically adsorbed water, as a result, on heating, the physically adsorbed water is evolved first and it requires a temperature of 180°C for the evolution of the H-bonded water. The evolution of water above 180°C is mainly due to the dehydroxylation by condensation of the surface hydroxyls. The dehydroxylation of surface silanols is almost complete at 500°C. It was observed that heating the laboratory gel to temperatures upto 500°C did not affect the surface area and pore diameter to any appreciable extent. At higher temperatures, beginning at 600°-700°C, the inner hydroxyl groups diffuse towards the surface resulting in sintering of the silica gel surface.

The removal of both types of water is necessary for reactions with the surface Si-OH groups and absorbents. The free hydroxyls or silanols have a physical attraction for atoms having lone electron pairs or π bonds in the molecule. They also preferentially attract compounds having hydrogen bonding capacity. High surface area of the high adsorption capacity, chromatographic grade silica gel accounts for the high degree of hydroxylation of the surface which is about 1.4 at 120°C, based on the calculation of Dzis'ko *et al*⁷, assuming that the complete coverage of the surface requires eight hydroxyl groups per square millimicron; resulting in a considerable amount of water being held on the silica gel surface by H-bonding and the primary adsorbed molecules act as centres for further condensation.

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Severe corrosion of stainless steel equipment has occurred in the decomposer units of a urea plant based upon the total recycle process. High carbon content of the stainless steel coupled with extensive carbide precipitation and high ferrite content in the weld metal appeared to be the factors responsible for the corrosion. Among the process conditions responsible for the attack were the high hydrogen sulphide content (about 10 ppm and above) and low oxygen (100 ppm) content in the feed carbon dioxide gas.

Corrosion of Urea Plant Equipment: A Case History

By K. M. VERMA, M. P. GUPTA, S. C. VARMA, H. GHOSH,
B. R. CHAKRAVORTY AND A. K. ROY,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Severe corrosion of stainless equipment has recently been observed in the decomposer units of the urea plant of Gorakhpur unit of Fertilizer Corporation of India. In this plant, urea is manufactured by the complete recycle process i.e. by reacting ammonia and carbon dioxide together with recycled liquor in a titanium lined reactor. The products leaving the reactor containing urea, carbamate and unreacted ammonia and carbon dioxide enter the decomposer units. The flashed gases from the first decomposer enter the low pressure decomposer and then to high pressure absorber cooler while the flashed gases from the second decomposer enter directly into the high pressure absorber cooler. The products from the high pressure absorber cooler are finally recycled to the reactor while the urea solution from the second decomposer is sent for further processing.

In the two decomposers steam at 180°C and 10 kg./cm.² pressure flow on the shell side and urea solution at 150°C and 35 kg./cm.² flow on the tube side/channel side in the decomposer I and at 155°C and 20 kg./cm.² pressure in the decomposer II. In the low pressure decomposer urea solution flows on the shell side at 150°C and 20 kg./cm.² pressure and decomposed gases on the tube side at 155°C and 35 kg./cm.² In the shell side of high pressure absorber cooler carbamate solution flows at 100°C and 20 kg./cm.²; cooling water flows on the tube side.

According to the manufacturers' specification the material of construction of channel side of the decomposers is SUS 33 (J. I. S.) clad steel; the inside separators are made of SUS 33. In the low pressure decom-

poser the material of the shell side is SUS 32 and of tube side SUS 33; in the high pressure absorber cooler, both the shell and tube sides are made of SUS 33 clad steel.

The first indication of trouble came from the colour of the urea solution which became pink. To investigate into the causes of the trouble a high pressure decomposer was opened up.

Visual Examination

Considerable thinning and loss of metal was observed on the stainless steel clad shell (channel side) and on the inside of stainless steel separators. The stainless steel cladding was covered with an adherent-reddish dark brown deposit. At some places the cladding had been completely eaten away. The inside separator pipe was also covered with the same type of deposit and the wall thickness had reduced to 1.5 to 2 mm. from an initial thickness of 3 mm. The weld metal appeared more or less unaffected while the parent metal on either side of the weld appeared deeply grooved, pitted and thinned.

After this examination some other equipment of the decomposer units were also opened up for examination. In all the equipments deep grooving, pitting and thinning of the material were observed and the surface was found to be covered with an adherent-reddish dark brown deposit. To find out the cause of corrosion, chemical analysis and metallographic examination were carried out with the samples available from various sections. The different samples studied and their chemical analysis are given in Table 1.

TABLE 1

Vessel component	Percentage composition			
	C	Mo	Cr	Ni
1. Decomposer bottom plate	.. 0.058	2.9	17.6	13.9
2. Decomposer base metal near the weld	.. 0.08	3.3	17.6	13.9
3. Low pressure decomposer high pressure side main body inside, A stream	.. —	2.7	16.9	14.0
4. High pressure decomposer I, A stream, top cover inside lining	.. —	2.4	17.2	12.9
5* High pressure decomposer I, A stream, top tube plate	.. 0.1	2.1	17.2	11.2
6. High pressure decomposer II, A stream, distributor wire mesh	.. 0.067	2.7	16.8	—
7. High pressure decomposer II, top cover lining, A stream	.. —	2.6	17.0	12.8
8. High pressure decomposer II distributor, A stream	.. 0.039	2.6	16.9	13.5
9* High pressure decomposer II, welded layer of top tube plate, A stream	.. —	—	—	—
10. High pressure decomposer I, separator, B stream	.. 0.08	2.2	16.7	14.5
11. High pressure decomposer II, separator, B stream	.. 0.08	2.9	18.2	14.0
12* High pressure absorber cooler, B stream	.. 0.08	2.8	—	—

*Samples 5, 9 and weld of sample 12 were strongly magnetic.

Metallographic Examination

Base Metal: The structure of the base metal in all the samples is austenitic with presence of slip bands. Extensive carbide precipitation is observed all along the grain boundaries and slip planes. Pits are present throughout but are more concentrated at or near the grain boundaries.

Weld Metal: The structure of weld metal in samples 5, 9 and 12 is dendritic with interdendritic segregation of carbide throughout the material. Pits are also abundantly present. The ferrite content of the weld metal in all the samples is higher than 2 per cent (in the range of 4 to 8 per cent).

Discussion

The analytical composition indicates that the samples of top tube plate of the first high pressure decomposer (A stream) and separator of the first high pressure decomposer (B stream) have less than usual molybdenum content; all the sample however correspond to type SUS 32 (J.I.S.) stainless steel. Metallographic examination has revealed extensive carbide precipitation all along the austenitic grain boundaries in the base metal and along the dendrites in the weld metal. This precipitation would have caused lowering of corrosion resistance of the material due to the depletion of chromium along the grain boundaries. This weakness at the grain boundaries is further confirmed by the presence of pits at or near them. The high ferrite content in the weld metal would have a detrimental effect as it is more prone to

attack by the urea carbamate system. Since the rate of diffusion of carbon is much faster in ferrite than in austenite, chromium carbide is precipitated in the austenite region close to ferrite with the consequent depletion of chromium in adjacent areas. This would explain the severe corrosive attack in areas adjacent to weld metal. In modern practice the ferrite content in the weld metal is usually kept within 2 per cent for service in the highly corrosive media in a urea plant and this limit has been exceeded in all the samples examined.

From a study of the process conditions prevailing in the plant, it has been observed that the permissible limit of hydrogen sulphide in the feed carbon dioxide gas had been 10 ppm and there were indications that the hydrogen sulphide had been much above the permissible limit at certain periods when the system for its removal was not working satisfactorily. Further, the oxygen which is essential for passivating the stainless steel in the particular corrosive environment, was kept in the feed gas at about 100 ppm—a rather low value according to usual standards. The high hydrogen sulphide content in the feed gas would have definitely consumed some oxygen, thus further lowering the effective oxygen concentration in the process stream.

Thus, the material whose corrosion resistance had already decreased due to the precipitation of chromium carbide and presence of high ferrite had suffered severe corrosive attack due to the extremely low oxygen concentration in the feed gas.

[Original mss. received on Sept. 8, 1970]

Studies on the urea-copper system reveal the formation of a 2:3 complex. At pH 5.8 with constant ionic strength, Cu^{2+} was observed to reduce gradually with increasing concentration of urea. The reaction is irreversible and the forward reaction rate K_f° has been evaluated. This provides an indirect method for the estimation of urea.

Polarographic Studies on the [Urea- Cu^{2+}] System: An Indirect Method for Estimation of Urea

By S. S. CHATTERJEE, M. B. MISHRA AND B. K. BANERJEE,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Urea, the most widely used nitrogenous fertilizer, has also been described as a ligand. However, the studies on the mode of its co-ordination are rather scarce. Two probable modes are through (i) $\text{C}=\text{O}$, the lone pair on oxygen atom being donated, or (ii) the —NH_2 , the lone pair on nitrogen atom being donated. In fact, Mizushima *et al*¹ have inferred from the infrared spectra of complexes of urea with Pd^{2+} , Pt^{2+} , Cu^{2+} and Zn^{2+} that urea coordinates through (i) $\text{C}=\text{O}$: oxygen with Cu^{2+} and Zn^{2+} , whereas, (ii) coordination in cases of Pd^{2+} and Pt^{2+} takes place through —NH_2 group. A Cr^{3+} complex of urea² has also been reported. However, no attempt has so far been made to study the electrochemical behaviour of urea on the dropping mercury electrode (d.m.e.). The present work was, therefore, undertaken with a view to study the same behaviour and find out an indirect polarographic method for the estimation of urea, as well as to evaluate the forward reaction rate, etc. The present paper records observations on the [urea —Cu^{2+}] system.

Experimental

All polarograms were recorded on an automatic recording polarograph* employing d.c. mode. A dipping annulus type cell was used and oxygen-free, dry nitrogen was bubbled through the cell mixture to remove the dissolved oxygen. The cell solution was kept in a nitrogenous atmosphere, with the help of a water-seal during the recording time. The height of the mercury reservoir

was the same except during diffusion control studies. All the measurements were done at $25 \pm 0.1^\circ\text{C}$. The capillary characteristics were as follows: $m=1.042$ mg./sec, $t=4.4$ sec, $m^{2/3} t^{1/6}=1.315$ $\text{mg}^{2/3} \text{ sec}^{-1/6}$; S.C.E. was used as a reference electrode.

Stock solutions of urea, copper sulphate and other reagents were made from B.D.H. (A.R.) grade chemicals and were used from time to time. The ionic strength of the cell mixture was kept constant throughout. Only double-distilled water was used for preparing the solutions.

pH measurements were carried out on a Phillips model PR9403 pH meter, which was standardized with potassium hydrogen phthalate (pH 4.0) and ammonia buffer (pH 9.0). The recorded curves have been analysed and plotted on a bigger scale (Fig. 1).

Results and Discussion

The effect of increasing concentrations of urea on the E , and height of the diffusion wave of Cu^{2+} in various media (supporting electrolyte) having pH 1.0 to 10.4 were studied and are tabulated in Table 1.

With pH between 4.4 and 10.0, the $E_{1/2}$ of Cu^{2+} wave shifts towards more negative potentials and the height of diffusion wave i_d decreases with the addition of increasing amounts of urea. It is evident from these data (Table 1) that complexation takes place only between pH 4.4 and 10.0.

The complexation studies were carried out in ammonium acetate + acetic acid media (pH 5.8) and

*Cambridge Univector Polarograph.

TABLE 1—EFFECT OF VARYING pH ON THE WAVE

Sl. No.	Media	pH	Shift in $E_{\frac{1}{2}}$	Shift in i_d	Remarks
1.	Sulphuric Acid	1.0	0.000	0.00	No complexation
2.	Acetate Buffer	4.4	Towards more-ve potentials	Decreases	Complexation takes place
3.	Potassium Nitrate	5.1	-do-	-do-	-do-
4.	Sodium Tartrate	8.0	-do-	-do-	-do-
5.	Ammonia Buffer	9.0	-do-	-do-	-do-
6.	Sodium Tartrate	10.4	0.00	0.00	No complexation

the results are given in Table 2. Except at very low concentrations of urea ($<0.100M$), the wave is irreversible. The value of the slope of $\log i/(i_d - i)$ vs E being 94 mV and that of the $\log (c)$ vs $E_{\frac{1}{2}}$ being 150 mv. This clearly indicates the irreversibility of the system, with a stoichiometry 2:3, metal ligand. However, the system is reversible at concentration of urea below 0.1M but the wave is not very well defined and hence is not suitable for stability constant evaluation.

The value of the transfer-coefficient, and the forward reaction rate K_f° was evaluated using the method of

$$\text{Matsuda and Ayabe}^3, \text{ i.e. } (E_{1/2})_C = \frac{0.06}{na} \left[\left(\log \frac{K_f^\circ}{\sqrt{D_N}} f_N + \frac{1}{2} \log \tau - 0.053 + \log \frac{i_1}{i_d} - (N-P) \log f_x C_x \right) \right] \quad (1)$$

where $0 < \alpha < 1$

where: $(E_{1/2})_C$ is the half-wave potential of the complex; α is the transfer co-efficient of the reduced form; K_f° is the forward reaction rate; D_N and f_N are the diffusion and activity co-efficients of the metal ion; τ is the drop time; $(N-P)$ is the stoichiometry; and f_x , C_x are activity coeff. and concentration of the ligand (urea). The value of α comes out to be 0.941 and that of the forward reaction rate 5.712×10^{-4} moles litre $^{-1}$ sec $^{-1}$. The

TABLE 2—COMPLEXATION STUDIES IN AMMONIUM ACETATE + ACETIC ACID (pH 5.8) MEDIA

Cell mixture: (A)			
(i)	0.4M Ammonium Acetate + Acetic Acid	..	10.00 ml.
(ii)	0.5% Gelatin	..	0.20 ml.
(iii)	Water	..	9.60 ml.
(iv)	Copper Sulphate solution	..	0.20 ml.
Total volume			.. 20.00 ml.
(B) pH of the resulting solution being 5.8			

(Concentration of Copper $\times 0.001M$)

Sl. No.	Conc. of Urea, M	$E_{\frac{1}{2}}$, volts	Diffusion Current, μA	Rever./ Irrev.	Log K_f°
1.	0.000	-0.035	30.000	Reversible	
2.	0.100	-0.040	27.000	Irreversible	
3.	0.200	-0.050	25.500	-do-	
4.	0.300	-0.060	23.750	-do-	
5.	0.400	-0.065	23.000	-do-	
6.	0.500	-0.065	22.000	-do-	5.712×10^{-4} moles litre. Sec.
7.	2.000	-0.160	15.000	-do-	

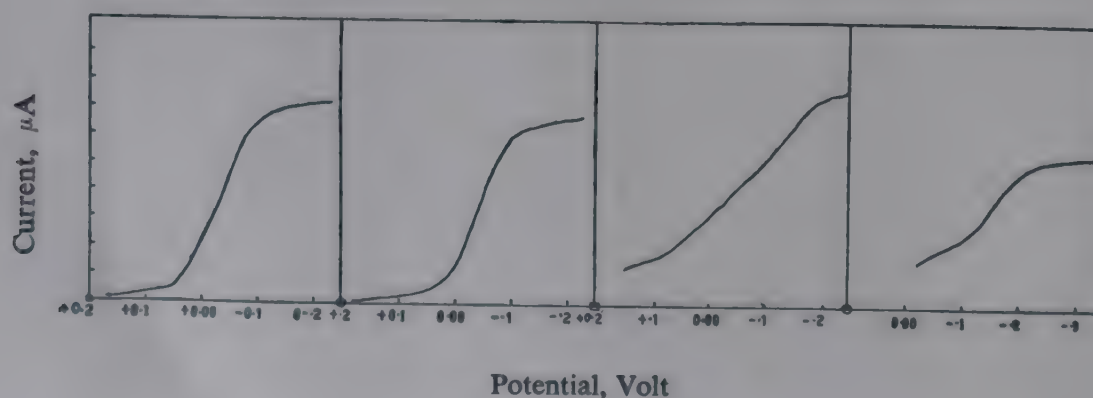


Fig. 1.

value of K°_f (5.712×10^{-4}) prove³ that the process is highly irreversible.

The decrease in wave-height of Cu^{2+} with the addition of increasing concentrations of urea is regular and has been utilized for the estimation of urea, keeping the concentration of Cu^{2+} and the media same, varying amounts of urea (in different concentration ranges) were added, and a calibration curve was plotted between the wave-height and urea concentration.

The wave was found to decrease regularly and a straight line plot was obtained. This is found to be a suitable method of estimating milli-, as well as macro-gram of urea in a sample. As is evident from the Table 3; the error is well within ± 1.0 per cent. The calibration curve is not given here. However, below milligram concentrations of urea, the wave is not very well-defined and therefore cannot be used for estimation purposes.

TABLE 3—ANALYTICAL RESULTS
(Concn. of Cu^{2+} = 0.001 M)

Sl. No.	Amount of Urea Added, g.	Amount of Urea Found, g.	% Error
1.	0.050	0.050	0.00
2.	0.100	0.099	-1.0
3.	0.200	0.2002	-0.1
4.	0.500	0.5003	+0.6
5.	1.000	0.9900	-1.0
6.	2.000	1.9897	-0.51

The height of the wave is directly proportional to the square root of the height of mercury reservoir. The reaction process is diffusion-controlled, and suitable for quantitative estimation.

At extremely low concentrations—say micro-amounts—the degree of association of urea and copper is different, and hence the plot of concentration of urea vs wave height of Cu^{2+} is not linear.

Biuret, though always associated with urea, does not interfere. It is known to form a complex^{4,5} with copper²⁺ above pH 9.0. Hence, the method is useful for estimating urea, in presence of biuret.

Conclusions

Urea is found to form a 2:3 complex with copper²⁺, in ammonium acetate + acetic acid medium (pH 5.8). The complex is reduced irreversibly at d.m.e. with a transfer coeff. (α) = 0.941 and $K^\circ_f = 5.712 \times 10^{-4}$ moles litre.⁻¹ sec.⁻¹ A suitable method for estimating urea, in presence of biuret in macro- or milligram amounts, is reported.

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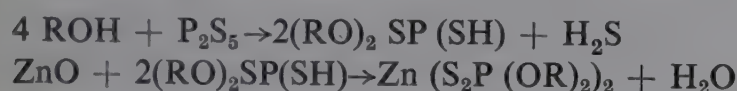
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Oxidation of Phosphorus Pentasulphide with Ceric Sulphate

By S. S. CHATTERJEE and B. K. BANERJEE,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Phosphorus pentasulphide is widely used for the production of oil additives, ore flotation agents, insecticides¹ etc. The major phosphorus compounds used as lubricant additives are the 0,0—dialkylphosphorodithioates², which are made by reacting alcohols with phosphorus pentasulphide according to the following equations.



These numerous applications of phosphorus pentasulphide in industry have necessitated standardization of aqueous phosphorus pentasulphide. This has been achieved by oxidizing it with ceric sulphate. In this communication, the general conditions for the oxidimetric determination of phosphorus sulphur compounds by ceric sulphate have been outlined and the results reported.

Experimental

Reagents: E Merck's guaranteed phosphorus pentasulphide was employed. A 0.005M stock solution was prepared by dissolving an accurately weighed quantity of phosphorus pentasulphate in an 1N aqueous solution of sodium hydroxide. This solution was standardized by subjecting aliquots to elemental analysis for sulphur³. Ceric sulphate was prepared by digesting the requisite amount of ceric ammonium sulphate in 2M sulphuric acid, which was then further standardized by titrating it against standard Mohr's salt solution using ferrion as an indicator⁴. Sulphuric acid used in these experiments was of AnalaR variety.

Procedure: An aliquot of phosphorus pentasulphide solution was taken in a conical flask and a known excess of ceric sulphate was added. Concentrated sulphuric

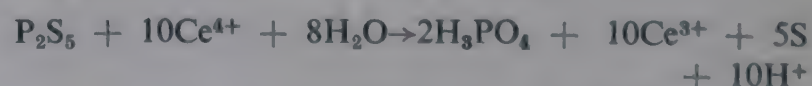
acid was added to maintain the overall acidity between 3 and 4M. The mixtures were kept aside at room temperature (28°C) for about 15 min. to ensure complete oxidation. Excess ceric sulphate was then back-titrated with a standard Mohr's salt solution using ferroin as an indicator. A blank titration was run simultaneously. From these observations the amount of ceric sulphate consumed during the oxidation and the molar equivalent of oxidant required per mole of phosphorus pentasulphide were calculated. The results of a set of experiments with different amounts of phosphorus pentasulphide are presented in Table 1.

TABLE 1

Phosphorus pentasulphide conc.	0.005 M
Ceric sulphate conc.	0.05 M
Overall acid conc.	3-4 M

P ₂ S ₅ Taken, ml	Ceric Sulphate Consumed. ml	Number of Equivalents of Oxidant Consumed per mole of P ₂ S ₅
1.0	1.01	10.10
2.0	2.00	10.00
3.0	3.01	10.03
4.0	4.02	10.05
5.0	5.01	10.02

The results (Table 1) show that 10 equivalents of ceric sulphate are required for 1 mole of phosphorus pentasulphate. Therefore, the following mechanism is suggested for the above oxidation scheme.



Thus, the equivalent weight of phosphorus penta-

sulphate under these conditions has been found to be one-tenth of the molecular weight. The oxidation was also carried out with boiling ceric sulphate under reflux but it did not show any encouraging results.

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A nomograph has been drawn on the basis of the equation $n\lambda = 2d \sin \theta$ for determining the (i) interplanar distances d vs 2θ and *vice versa* for any characteristic radiation of the target element, such as molybdenum, copper, cobalt, iron and chromium element (iii) to two-theta (2θ) and *vice versa* for the appropriate series and line for the crystals, Topaz, lithium fluoride, sodium chloride, EDDT and ADP, used in X-ray fluorescent spectrometer.

Nomograph for X-Ray Diffraction and X-Ray Spectroscopy

By V. K. SRINIVASA AND B. K. BANERJEE,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Description

The equation used in drawing the nomograph is the well-known Bragg equation

$$n\lambda = 2d \sin \theta,$$

where n = order of reflection (in this case = 1)

λ = wave length of the characteristic radiation of the target element, Å

d = interplanar distance, Å

θ = Bragg angle.

The unique advantage of this nomograph is that it can be used for any value of λ used in x-ray diffraction technique to give instant answers to d vs 2θ and *vice versa*. Also, this nomograph can be used to determine various elements from magnesium to uranium against two-theta values under the appropriate series and lines—($K\alpha$, $K\beta$, $L\alpha$, and $L\beta$, etc)—for different crystals, such as Topaz, lithium fluoride, sodium chloride, EDDT and ADP, currently used in x-ray fluorescent spectrometer.

The nomograph (Fig. 1) is divided into two sections—the left-hand side is used in conjunction with x-ray fluorescent spectrometer and the right-hand side for x-ray diffraction technique.

To obtain the d spacing against the value of 2θ for a particular target element of characteristic radiation ($K\alpha$ or $K\beta$ of Mo, Cu, Co, Fe or Cr), draw a straight line connecting the target point at the centre on the right-hand side portion of the nomograph and the known value of 2θ on the central scale. The point where this straight line strikes the d scale at the extreme end, on the right hand side, gives the value of d Å. Hence, of the three variables λ , d and θ , if any two are known, the corresponding value of the third can be found by simply drawing a straight line through the two given points and reading the value of the point where it crosses the third scale. The accuracy of the readings at lower angles is about ± 3 per cent and at higher angles about ± 0.5 per cent.

ELEMENT

U	92
TH	90
FR	88
PO	84
PA	82
FL	80
HO	78
PT	77
OS	76
RE	75
W	74
TA	73
HF	72
LU	71
YB	70
TM	69
ER	68
HO	67
DY	66
TB	65
GD	64
EU	63
SM	62
TL	61
NO	60
PR	59
CE	58
LA	57
BA	56
CG	55
XE	54
I	53
TE	52
SB	51
SN	50
IN	49
CD	48
AG	47
PD	46
RH	45
RU	44
TC	43
MO	42
NB	41
ZR	40
Y	39
SR	38
RB	37
KR	36
BR	35
SE	34
AS	33
GE	32
GA	31
ZN	30
CU	29
NI	28
CO	27
FE	26
MN	25
CR	24
V	23
TI	22
SE	21
CA	20
K	19
A	18
CL	17
S	16
P	15
SI	14
AL	13
MG	12

TOPAZ L_{β}	+	TOPAZ L_{α}
LIF L_{β}	+	LIF L_{α}
NACL L_{β}	+	NACL L_{α}
EDDT L_{β}	+	EDDT L_{α}
ADP L_{β}	+	ADP L_{α}
TOPAZ K_{β}	+	TOPAZ K_{α}
LIF K_{β}	+	LIF K_{α}
NACL K_{β}	+	NACL K_{α}
EDDT K_{β}	+	EDDT K_{α}
ADP K_{β}	+	ADP K_{α}

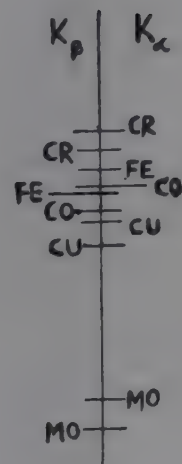
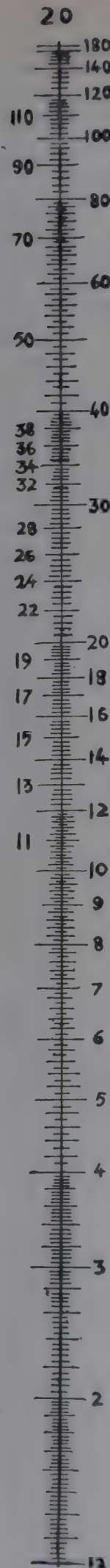


Fig. 1—Nomograph

Used in conjunction with the x-ray fluorescent spectrometer, the left-hand side portion of the nomograph enables to find two-theta values for various elements under appropriate series and lines for the crystals such as Topaz, lithium fluorides, sodium chloride, EDDT and ADP. To find 2θ value for an element under an appropriate series and line, connect the crystal point marked at the centre and the point referring the particular element on the scale at the extreme end of the left-hand side. The point where this straight line crosses the central scale gives the value of 2θ . Similarly, if the value of 2θ and the series and line of the crystal used are known, the element in question can be determined by simply connecting these two points and extending this line to cross the third scale on which the positions of

various elements are marked. The point where this straight line strikes, the element in question is found out.

Acknowledgement

Thanks are due to Sri S. N. Parameshwar, Mechanical Engineer, P & D Division, for helpful suggestions to draw the nomograph.

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The maximum penetration of β -particles of energy 1.17 MeV in aluminium is determined and found to be 446 mg/cm². It is suggested that aluminium can very well be used in the construction of β -shells and β -glove boxes in place of imported perspex sheets or any other material.

Aluminium as a Cheap Shielding Material for Pure *Beta*-Emitters

By INDU SHEKHAR MISHRA AND T. SAHU,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

β -sources are widely used in various industries for quality as well as process control. To ensure safety for high energy β -emitting sources shielding is essential¹, though not so much for weak β -emitters. The absorption of β -rays by a substance produces 'Bremsstrahlung' having characteristics of soft x-rays², additional shielding of low atomic number material is required to minimise the amount of Bremsstrahlung. The absorption of β -particles in an absorber is of complex nature due to (i) elastic and inelastic scattering leading to much straggling (ii) the energy spectrum of β -particles is continuous from zero up to some definite maximum ($E_{\max}$) for each

β -source and therefore not monoenergetic. The existence of a continuous spectrum is explained by emission of a neutrino³ with each β -decay which carries away an amount of energy ΔE such that $\Delta E = E_{\max} - E$ where E = energy of the emitted electron.

β -particles interact with both the electrons and nuclei of substances. The interactions are either elastic or inelastic. In elastic scattering β -particles do not lose any energy but they merely undergo sharp changes in direction and hence are scattered. But if the β -particles collide with the extranuclear electrons, inelastic scattering takes place and the energy of the impinging β -particles is lost

in producing ionization (ionization losses). The ratio between these two losses is given approximately by $1000/ZE$ where E = energy of the β -rays measured in MeV, and Z = atomic number of the absorbing material. Thus, if Z and E are increased the ionization losses are reduced with respect to those due to radiation only. The penetration of β -particles into a substance depends on magnitude of these losses. If a β -particle is having energy E_{max} (MeV), the path length in any substance may be determined from the approximate empirical formula—

$$(1.205 - 0.0954 \ln E_{\text{max}})$$

$$1 \rho_{\text{max}} = \rho d = 0.412 E_{\text{max}}$$

where ρ = density of the substance, g/cm³
 d = thickness of the substance, cm.
 $1 \rho_{\text{max}}$ = penetration, g/cm²

The range of β -particles is as high as several metres in gases, and only a few millimetres in solids and liquids. For an absorber like aluminium it has been empirically established that the range (R) of β -particles is given by $R_{\text{max}} = 0.542 E_{\text{max}} - 0.133$ where R_{max} = Maximum range in mg./cm² and E_{max} = Maximum Energy of β -particles in MeV.

Experimental

The equipments used were Trombay-make electronic instruments, such as (1) decade scalar (DS 325), (2) preset timer (ET 450A) and (3) self-quenched GM tube I 1050. The source was the standard Ra—DEF emitting β -particles of energy 1.17 MeV having abundance 100 per cent and activity 0.029 μC . The set-up (Fig. 1) was tested for the 50 cycle test and an average count rate of 3002 counts/min. showed that equipments were ready for further operation. The average background count rate was found to be 25 counts/min. and the average count rate with bare source 540 counts/min. The count rate for each standardized aluminium absorber of gradually higher thickness was taken till the count rate was found to be the least. All the readings

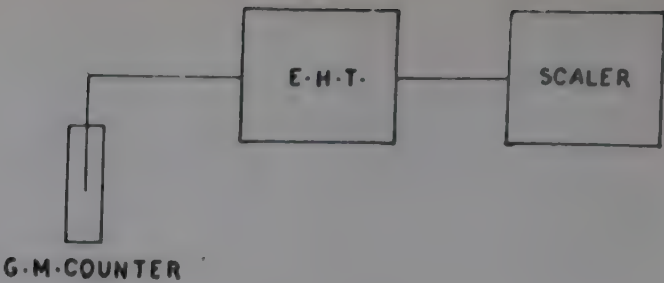
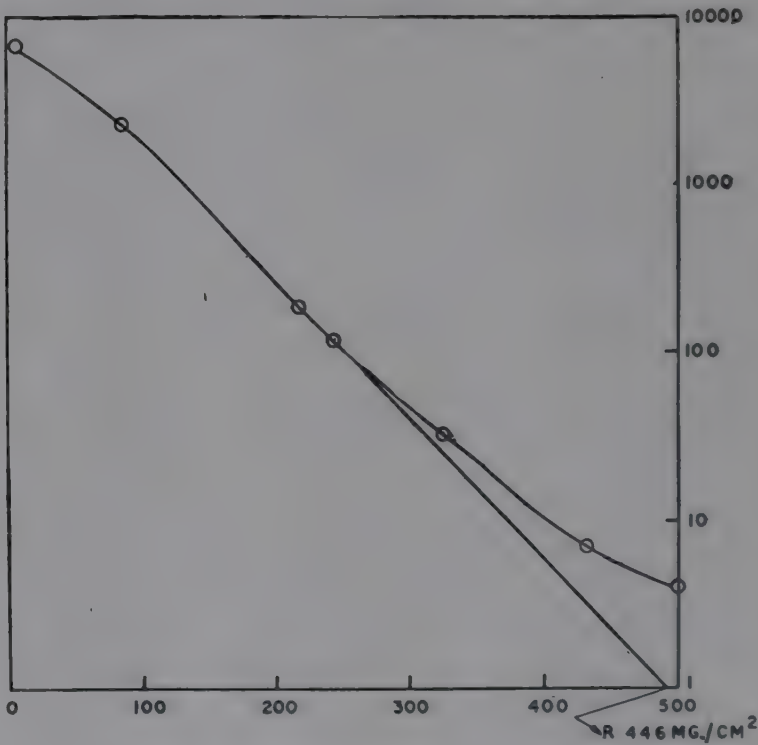


Fig. 1—Experimental Set-up

were tabulated and calculations were made as follows: Since density of air at N.T.P. = 0.001293 g./cm.³ therefore 2 cm. length of airways is equivalent to 2.5 mg./cm².

A graph of corrected count rate/min. against the absorber thickness in mg./cm² was plotted and by extrapolating the line, the maximum range (R'_{max}) of β -particle in aluminium was found to be 446 mg./cm.² (Fig. 2).



Corrected Absorber Thickness, mg/cm²
 Fig 2

Actual Absorber Thick- ness, mg./cm ²	Corrected Absorber Thickness, mg./cm ²	Count Rate/min.	True Count Rate/min.	Correction from Graph	Corrected Count Rate/min.
0.0	5.0	6837	6812	275	7087
84.5	89.5	2410	2385	15	2400
219.0	224.0	216	191	1	192
243.0	248.0	143	118	0	118
324.0	329.0	60	35	0	35
432.0	437.0	31	6	0	6
540.0	545.0	29	4	0	4

For the construction of β -boxes for radioisotopes emitting β -particles of energy 1.17 MeV or less, in order to ensure maximum safety aluminium sheets having thickness 10 mg./cm² to 15 mg./cm² more than 446 mg./cm² can be used. This additional thickness would minimize the 'Bremsstrahlung' soft x-rays hazards also which is produced by the absorption of β -particle in absorbing material aluminium in addition to complete absorption of all the Betas. Most effectively the 'Bremsstrahlung' so produced can be minimised by coating aluminium sheet with any low Z material.

It is to be noted that higher the energy of the β -particle, more will be its range and therefore it is quite essential that maximum range for each β -emitting radioiso-

tope be determined and then β -boxes or β -shells for that isotope be constructed. Therefore aluminium can be used for β -boxes and β -shells instead of costly imported perspex or any other material which is costlier than aluminium.

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A simple method for rapid estimation of ammonia in gaseous samples has been developed. It is based on absorption of ammonia in acidic solutions and the results are comparable to those obtained by titration.

Rapid Determination of Ammonia in Gases

By V. C. RAI,

*Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar*

Rapid quantitative estimation of ammonia in gases is of considerable importance in most of the unit processes that require monitoring, recovery and sometimes recycling of gaseous ammonia. Several titrimetric, colorimetric, chromatographic, conductometric and spectrophotometric techniques have been reported¹⁻¹⁸ and are being used in research and industry. All these methods are time-consuming and/or require expensive equipment as well as some technical skill. Titration is perhaps the most reliable and simple method for determining a wide range of ammonia concentrations. This paper presents a rapid and simple method for the determination of ammonia in gases which may be of practical interest.

Based on direct absorption, the method requires a burette, a levelling bottle, rubber-tubings and a gas syringe for sampling. The burette has to be slightly modified to incorporate a rubber septum by joining a Y connector to its open end (Fig. 1). The burette is held in an inverted position and its open end is connected to the levelling bottle with rubber-tubing. The levelling bottle is mounted at a height slightly above the capillary end of the burette.

The system is filled with an acidic solution (5 per cent hydrochloric acid was used), the liquid level in the levelling bottle adjusted just above the stopcock of the burette and the stopcock is then closed. The gas syringe

is dried and repeatedly flushed with the gas sample. An accurately measured sample of gas (20 ml.) is then slowly injected into the burette through the rubber septum. As the gas bubbles rise in the burette, ammonia is absorbed by the acidic solution and unabsorbed gas collects at the top. The levelling bottle is lowered till the liquid level in the bottle coincides with the level in the burette. The liquid level in the burette plus the volume of unmarked but previously calibrated portion gives the volume of ammonia-free gas. Assuming complete absorption of ammonia in the liquid, the ammonia content of the original gas sample can now easily be calculated.

The validity and accuracy of the direct absorption method were tested experimentally by comparing the results of this method with titration results. Air-ammonia mixtures containing about 4 to 27 per cent ammonia by volume were prepared and tested with this method. The acid solution in the burette was renewed after each injection. However, with low ammonia concentrations the same solution was found to give acceptable results for as many as 5 to 8 injections. The frequency of replacement of acid solution is dependent on ammonia concentration and the acidity of the solution*. The gas samples were also tested by titration. 20 ml. of gas sample was injected slowly in 20 ml. of 0.1N sulphuric acid with constant stirring so as to assure complete absorption of ammonia. The solution was then titrated against sodium hydroxide, using a mixed indicator containing methyl red and methylene blue. A blank titration was also performed in which no gas was injected in the acid. From these, the amount of ammonia was calculated in g. moles and then converted into volume at room temperature assuming ideal gas behaviour, which was then used to compute the volume percentage of ammonia in the original gas sample. The ammonia content of gas samples, obtained by the direct absorption method and titration methods, were plotted on a linear graph (Fig. 2), which shows a very close agreement between the two sets of results.

There is very little scatter from the line of unit slope in Fig. 2. The deviation from the titration values is within ± 0.5 per cent and could be attributed to experimental error in the direct absorption method or in the titration method itself. The direct absorption requires less than a minute to find out the ammonia content of a

*Some indicator may be added to the acid solution which would indicate the exhaustion of the acid by absorption of ammonia by a change in colour. The coloured solution would also be helpful in reading liquid levels in the burette.

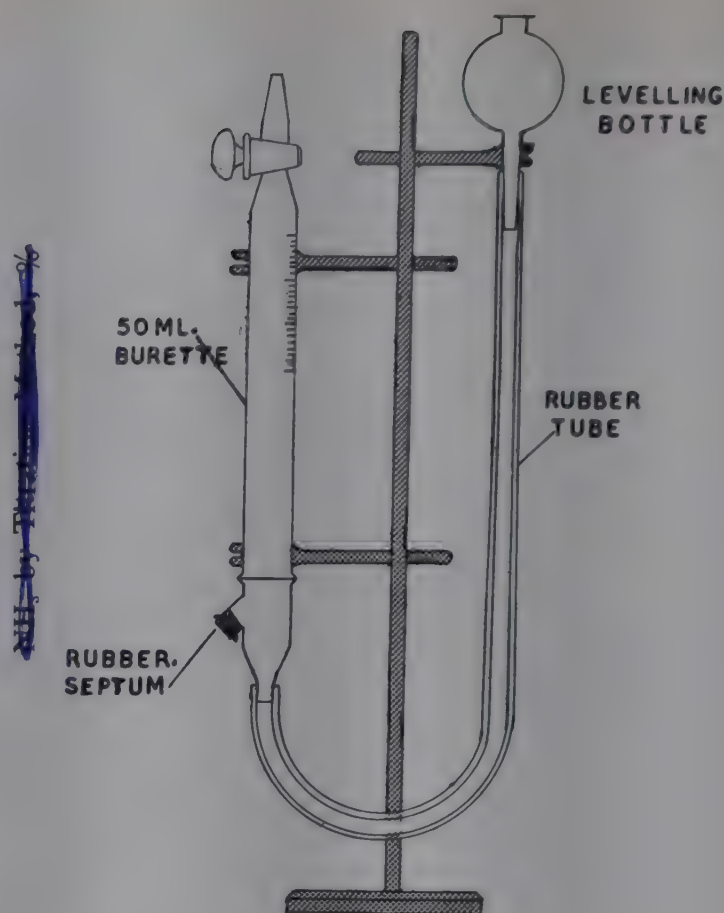


Fig. 1—Ammonia Estimation Apparatus

gas sample as against a minimum of 10 min. by titration.

The direct absorption suffers from the same limitations as the titration method, viz. that there should be no other acid-soluble component in the gas and that the moisture content of the gas should not be too high, otherwise it may condense in the syringe and retain

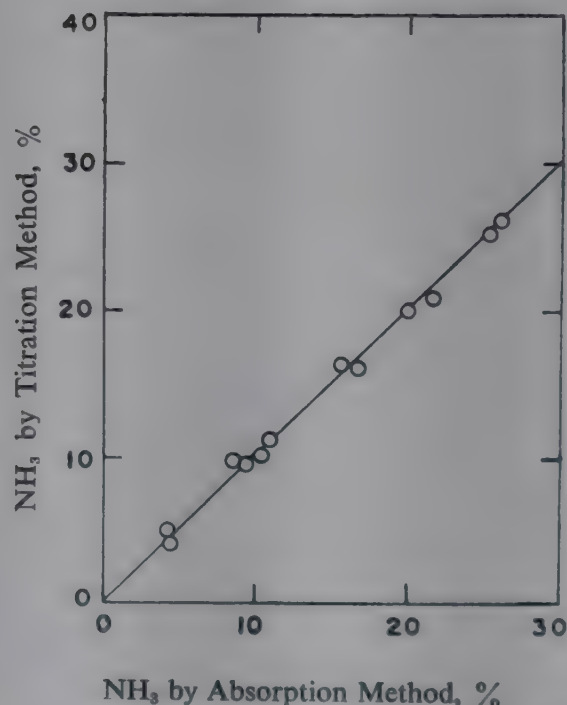


Fig. 2—Ammonia Determination in Gas by Titration and Absorption Methods

some ammonia. Moreover, the ammonia content of the sample must be high enough to give an appreciable difference in volume.

The apparatus may further be improved by using a gas burette enclosed in a water jacket to avoid temperature variation while measuring gas volumes and by calibrating it to give ammonia content in the gas directly for a particular volume of sample injected.

The direct absorption method could be used for estimation of ammonia in gas streams in ammonia, nitric acid and fertilizer plants as well as in research where a rapid but not very precise method is required.

Acknowledgement

This investigation was initially carried out by the author when he was working with the Research Council of Alberta, Edmonton, Canada (1966-67). He is grateful to its Director, Dr. E. J. Wiggins, for his consent to publish this note.

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The compounds, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ and $\text{Pb}_9(\text{PO}_4)_6$ have been prepared from aqueous solutions. The powder diffraction patterns show that the water-stable compounds have the apatitic structure. There are detectable differences in the relative intensities and spacings of the x-ray patterns of each compound.

Preparation, Lattice Parameters and X-Ray Powder Patterns of Lead Apatites

By VIJAY MOHAN BHATNAGAR,*

*Faculte des Sciences de Toulouse,
38 rue des 36 Ponts, Toulouse (France)*

The apatites are important phosphate minerals. The preparations of lead hydroxyapatite, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$, and lead phosphate, $\text{Pb}_9(\text{PO}_4)_6$, are reported in this note. A commercial sample of lead phosphate was also investigated. Its unit cell dimensions corresponded to a defect-hydroxyapatite. The x-ray powder diffraction patterns were obtained with a Geigerflex x-ray diffractometer.

Lead Hydroxyapatite [$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$]: A solution of K_2HPO_4 (0.96 g./100 ml.) was added dropwise to a refluxing solution of $\text{Pb}(\text{CH}_3\text{COO})_2$ (2.00 g./100 ml.). The whole mixture was continuously stirred for about 45 hours, keeping the temperature of the reacting solution at about 100°C. The precipitate was filtered, washed with distilled water and dried at 100°C.

The following cell constants were found for this apatite: $a=9.85\text{\AA}$, $c=7.40\text{\AA}$, and $c/a=0.751$. The x-ray powder diffraction data are given below (Table 1):

Lead Hydroxyapatite [$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$]: A solution of Na_2HPO_4 (6.00 g./350 ml.) was added dropwise to a continuously stirred solution of $\text{Pb}(\text{CH}_3\text{COO})_2$ (15.00 g./300 ml.) at about 100°C. The solution was stirred for about 29 hours, filtered, washed with distilled water and dried at 100°C.

The following lengths of a and c axes were found: $a=9.88\text{\AA}$, $c=7.41\text{\AA}$, and $c/a=0.750$. The x-ray powder diffraction patterns are given below (Table 2).

TABLE 1—X-RAY POWDER DIFFRACTION PATTERNS OF LEAD HYDROXYAPATITE

dÅ	I/I ₀	hkl	dÅ	I/I ₀	hkl
4.98	6	110	2.26	10	302
4.31	26	200	2.23	9	113
4.15	23	111	2.15	7	400
3.77	4	002	2.07	29	222
3.44	21	102	2.01	16	312
3.27	39	210	1.97	21	213
3.15	13	—	1.87	31	321
3.08	7	—	1.62	11	420,214
2.99	100	211	1.56	11	304,502
2.88	47	300	1.52	13	510
2.78	7	—	1.51	17	511

TABLE 2—X-RAY POWDER DIFFRACTION PATTERNS OF LEAD HYDROXYAPATITE

dÅ	I/I ₀	hkl	dÅ	I/I ₀	hkl
4.93	5	110	2.15	8	400
4.29	20	200	2.06	20	222
4.13	27	111	2.00	14	312
3.72	8	002	1.97	20	213
3.41	31	102	1.90	15	321
3.24	29	210	1.86	27	303,410,004
2.93	100	211	1.61	10	420,214
2.86	32	300	1.56	10	304,502
2.26	5	302	1.54	6	510
2.22	10	113	1.51	10	511

*Present address: P.O. Box 399, Cornwall, Ontario (Canada).

Commercial Lead Phosphate $[\text{Pb}_3(\text{PO}_4)_2]$: The purified commercial sample of lead phosphate was obtained from Matheson, Coleman, and Bell Co. Its x-ray pattern was that of an apatite. Its method of preparation was unknown as the supplier declared it as a classified work. It was a 1962 sample listed in their catalogue as $\text{Pb}_3(\text{PO}_4)_2$. Its unit cell dimensions were found as $a=9.81\text{\AA}$, $c=7.25\text{\AA}$, and $c/a=0.739$. The x-ray powder diffraction results are presented below (Table 3).

TABLE 3—X-RAY POWDER DIFFRACTION PATTERNS OF COMMERCIAL LEAD PHOSPHATE

dÅ	I/I ₀	dÅ	I/I ₀
4.27	38	2.03	20
4.08	48	1.97	14
3.49	14	—	—
3.25	20	1.94	18
3.22	35	1.88	22
2.93	100	1.85	14
2.83	51	1.83	17
2.17	12	1.59	7
2.13	10	1.52	13
		1.49	10

Lead Phosphate $[\text{Pb}_3(\text{PO}_4)_2]$ A method similar to Alders and Stahler's¹ was followed. The $\text{Pb}(\text{CH}_3\text{COO})_2$ solution (2.56 g./100 ml.) was added dropwise to a continuously stirred solution of Na_2HPO_4 (5.76 g./150 ml.) at about 100°C. The whole reaction was stirred for about 24 hours, filtered, washed with distilled water and dried at 100°C.

The cell constants of this product were: $a=9.75\text{\AA}$, $c=7.20\text{\AA}$ and $c/a=0.738$. The x-ray powder diffraction data are shown below (Table 4):

TABLE 4—X-RAY POWDER DIFFRACTION PATTERNS OF LEAD PHOSPHATE $\text{Pb}_3(\text{PO}_4)_2$

dÅ	I/I ₀	hkl	dÅ	I/I ₀	hkl
4.44	24	200	2.03	20	222
4.08	47	111	1.97	16	312
3.63	22	002,201	1.93	24	213
3.47	22	102	1.87	24	321
3.22	31	210	1.83	27	—
2.93	100	112,211	1.52	10	—
2.83	41	300	1.49	16	—
2.16	18	113			
2.12	12	203			

Acknowledgements

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An Improved Process* for Preparation of Ammonium Sulphamate—A Weedicide

By A. SINHA, T. K. K. ACHARI, K. C. DATTA,
G. S. KHERA AND R. N. METIA,

*Planning & Development Division,
The Fertilizer Corporation of India Ltd, Sindri, Bihar*

Ammonium sulphamate is a potential weedicide and fire-proofing agent. It is effective in killing vegetation when sprayed in concentration of 0.2 per cent in water. It is also used in metal cleaning and electro-plating. It is sprayed on communication lines, like telephone poles, etc., to prevent wild creepers and other plants climbing over them and creating problems for communication lines. It finds extensive use in defence establishments particularly for the prevention of wild growths over under-ground fuel dumps, which are required to be maintained free of weeds to prevent from fire-hazards.

As this product is not available indigenously, its use has been limited. Recently one commercial firm has reported its manufacture on a small scale. With the availability of this product, its use by Railways and Defence establishments and in areas around factories is bound to increase.

Experimental

The raw materials required for the production of ammonium sulphamate are urea and high concentration sulphuric acid.

The synthesis of ammonium sulphamate comprises

two steps, viz. (i) preparation of sulphamic acid, (ii) neutralization of sulphamic acid with ammonia to form ammonium sulphamate. In the experimental procedure urea is made to react with a high concentration sulphuric acid and the details of the process know-how for the manufacture of ammonium sulphamate are covered by patent rights in various countries¹⁻⁴. In the process know-how, developed in this laboratory, the maximum yield of ammonium sulphamate obtained is 95 per cent, which is much higher as compared to the yield of the product by other known processes. Further, the concentration of sulphuric acid used in the process is lower than that reported. The product obtained is of high purity and stability as determined by physical and chemical tests.

The process know-how has been developed and bench-scale preparation has been carried out. It is being scaled up from bench-scale to semi-pilot plant.

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*applied for patent.

[Original mss. received on Sept. 21, 1970]

Technical Digests

An Improved Method for Preparation of Phosphorus Pentasulphide

Phosphorus pentasulphide is the important intermediate product in the manufacture of a large number of insecticides and organophosphorus chemicals. Besides, it finds extensive use in the production of oil additives, ore flotation agents and manufacture of phosphate esters. In this improved patented process a stainless steel cup is filled with an intimate mixture of red phosphorus and sulphur and covered with an inverted similar cup having slightly larger diameter so as to exclude the presence of air over the reaction mixture. The cup is heated in an air-oven for 2-3 hours at a temperature ranging between 140 and 160°C during which the mixture melts and reaction takes place. The product is cooled slowly to room temperature and the reacted hardened mass is taken out, ground and pulverized. It is then repeatedly extracted with hot carbon disulphide in order to remove unreacted elements till the product attains specific gravity 2.03.

In this improved process the yield of pure phosphorus pentasulphide is 70 per cent on the basis of total quantities of reactants taken and the product is of very high purity as determined by x-ray diffraction technique when no impurity is detected.

[*Ind. Pat. No. 114901*, by T. K. K. Achari & A. Sinha, P & D Div., FCI, Ltd.]

An Improved Process for Preparation of High Adsorption Capacity Silica Gel

Silica gel of specific grade (Davison code 922 and 923) only is recommended for authentic separation and quantitative estimation of paraffins, naphthenes, aromatics and olefins. This improved patented process produces a high adsorption capacity silica gel from indigenously available raw materials at reasonably cheaper rate and gives superior performance characteristics than the imported silica gel. A clear solution of sodium silicate in hot distilled water is prepared and this hot solution is poured into equal volume of 10 per cent by volume of fuming hydrochloric acid. The mixture is agitated with a suitable mixer so that the

average temperature of the solution is between 50 and 55°C and pH between 1.0 and 1.5. The aqueous acid silicate mixture is gelated with the aid of hydrofluoric acid. This decreases the setting time for gelation from 200 hours in earlier cases to 3 to 4 hours in the improved method and still retains as high a surface area as 811 m²/g and increases adsorption capacity. Solidified mass is cut into pieces and boiled with water. The wash solution is discarded and the wet heat treatment is continued till pH of the extract approximates 2.0 to 2.5. Washed solid is kept at room temperature (25 to 28°C) for partial slow drying which takes nearly 50 hours. The gelated mass is then boiled in 0.1N hydrochloric acid and rewashed with distilled water (preferably with de-ionized water) till the pH of the extract is raised to 4.0. This wet gel is kept in an oven at 200°C and gradually the oven temperature is reduced and after the gel is perfectly dried it is packed in air-tight wide mouth containers while still hot. The yield of the high adsorption capacity silica gel is 50 per cent by weight of sodium silicate taken.

[*Ind. Pat. No. 113944* by R. N. Shukla, A. R. K. Sarma, P. K. Mukherjee and A. Sinha, P & D Div., FCI Ltd.]

Fertilizer Technology and Know-How in India

India is in a position to build fertilizer plants with her own know-how, designing and engineering. She is also in a position to supply catalysts, equipment and machinery for fertilizer plants and to collaborate with other developing countries which are planning to establish fertilizer industry on the basis of mutual benefits, thus observed Sri. L. M. Joshi of Planning and Development Division of FCI Ltd., at Petrochemical seminar organized by Iran Exhibition Organisation, Teheran. In a paper* presented to the seminar he pointed out the fertilizer requirements of the country. He told the gathering that Indian fertilizer industry is two decades old and earlier projects were executed on turn-key basis by foreign parties. But with the advent of Fertilizer Corporation of

*Status and Development in Fertilizer Technology and Know-how in India, presented at Teheran (Iran) during Oct. 12-17, 1969.

India Ltd., and Fertilizer & Chemicals Travancore Ltd., India started generating its own know-how. Planning including the assessment of requirement of various types of fertilizers, choice of product pattern and process sequences in relation to the raw materials and utilities available, preparation of techno-economic feasibility studies and detailed project reports, investment analysis etc., are undertaken within the country without any outside help. The Planning and Development Division of FCI has been actively associated with these activities for almost all the major fertilizer plants in India. For developing the process know-how and technological design, basic and applied research is essential. This is necessary not only to develop new processes but to improve the existing ones. The P & D Division has, therefore, been organized as a comprehensive organization providing excellent research/development facilities for development of know-how and providing adequate support for its planning/process design/engineering functions. This Division can now undertake work for ammonia, ammonium sulphate, nitric acid, calcium ammonium nitrate, urea and catalysts.

The speaker explained the status of mechanical equipment and machinery, electrical equipments and instruments. In his view considerable progress has been made in India in recent years to establish fabrication facilities for equipment machinery needed in fertilizer industry. Indian fabrications are supplying about 70-75 per cent of the total tonnage that goes to build a fertilizer plant. In case of vendor's equipment, about 45-55 per cent of the items are available within the country. In the field of pipings and fittings about 75-80 per cent of the material is procured within the country. The specialized areas in which equipment/machineries are to be imported, and not yet fabricated in the country are: (i) high pressure vessels like ammonia and urea reactors and other high pressure equipment in the ammonia synthesis train; (ii) high pressure gas compressors, (iii) high pressure pumps, reciprocating pumps and some special pumps like carbamate and ammonia charge pumps for urea plant; and (iv) high pressure pipes, fittings and valves. Expertise is being acquired by some state-owned fabricators for fabrication of very high pressure vessels, and high pressure centrifugal and reciprocating compressors. The additional facilities are likely to be completed by 1971-72 after which India will be in a position to obtain from within the country 85-90 per cent of her needs in this field. The chemical industry, in general, and fertilizer industry, in particular, require quite a substantial quantity of alloy steel and stainless steel sheets and plates, tubes, flanges, etc. The value of these items is estimated to be more than a million

dollars in a large fertilizer plant. The production of alloy steel and stainless sheets and plates has now been taken up and it is hoped that the country's requirement in this field will be met after 1971-72.

The Indian electrical engineering industry is now supplying about 80-85 per cent of the requirements of the fertilizer industry. Some very specialised equipment that are being imported include automatic voltage control equipment, explosion proof equipment, dust and hose proof equipment and some specialized components for motors.

Indian industries in the instrument field are in a position to supply 70-75 per cent of the total value of the process instruments required in fertilizer industry. There are instruments manufacturing units both in public and private sectors which can supply many types of modern process instruments. Small scale industries have also taken up the manufacture of bimetal thermometers, industrial thermometers, alarms and safety systems. However, the fertilizer and chemical industry has to import special types of instruments such as process analysers, large control valves, magnetic flow meters, gauge glasses, etc.

Air-borne Radioactivity at Sindri

With the commissioning of a full-fledged Radio-Isotope Laboratory, a non-destructive testing unit using radio-nuclides and a 1000-Curie Gamma garden at Sindri, a measurement of radio-active contamination of the locality has been carried out. In a paper*, read at the National Symposium on Radiation Physics held at the Bhabha Atomic Research Centre, Trombay during Nov. 24-27, 1970, survey data at 22 different locations (Fig. 1) of Sindri covering a radial distance of 4.5 km. around the Radio-isotope laboratory during February to August 1970 have been presented.

The atmospheric radioactivity is partly due to the presence of long-lived fall-out particles and partly to cosmic rays and other naturally occurring radioactive elements, e.g. radon and thoron gases. The solid disintegration products of these gases, viz. Ra (B & C), ThB, etc., attach themselves to the aerosoles and condensation droplets which can be collected by arresting particles by suction of air through fine grain filter paper and along with rain water. The environmental radioactivity can be assessed effectively by collecting the atmospheric dust particles by sucking a known volume of air

*Air-borne Radioactivity at Sindri by S. C. Srivastava, S. P. Khalsa, S. K. Das & K. C. Banerji, P & D Division, FCI Ltd.



Fig. 1—Map of Sindri showing the position of sampling points

[Scale 1 cm. = 1200 m.]

through filter paper. The contribution due to short-lived natural nuclides can be estimated by measuring activity of the sample immediately thereafter. The measurements were done immediately after sampling and also after a gap of 3 days. The general γ background of the locality was found more or less constant and was measured in terms of dose-rate corresponding to cobalt-60 γ rays.

The daily variation of gross β -activity of the air samples collected at the Radio-Isotope Laboratory during February to July 1970 has been shown in Fig. 2. The study has shown that short-lived β -components were mainly due to radium (B and C) and thorium (B). The concentration of the long-lived particles and the general γ background are given in Table 1. The concentration of thoron in the atmosphere has been found to be much

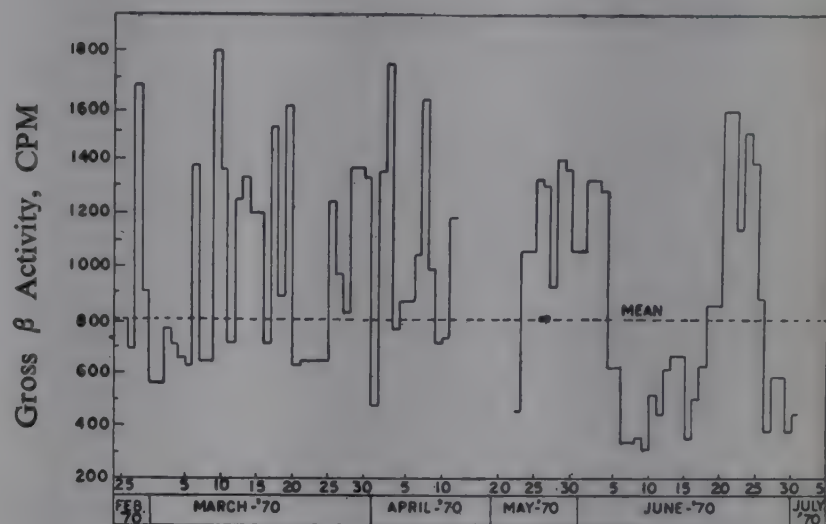


Fig. 2—Daily Variation of Gross β Activity in Air
Distance, metre

TABLE 1—CONCENTRATION OF LONG-LIVED PARTICLES & THE GENERAL BACKGROUND

S. No. of Sampling Point	Location of Sampling Points	Sampling Date	Distance from R.I. Lab., metres	Concentration, $\mu\mu\text{ci}/\text{m}^3$ of air			General background $\mu\text{r}/\text{hr}$
				Radon	Thoron	Long-lived	
1.	Radio-Isotope Lab.	4-7-70	0	22.4	—	6.5	7.5
2.	New Pilot Plants	5-7-70	201	54.6	—	7.5	6.2
3.	Agronomical Research Wing	6-7-70	320	22.4	—	5.0	5.8
4.	Sindri Post Office	7-7-70	755	32.1	—	6.5	6.5
5.	F.C.I. Factory	9-7-70	830	32.5	—	8.0	8.0
6.	A.C.C. Colony Area	10-7-70	868	18.6	—	4.5	4.0
7.	F.D. Bungalow Area	13-7-70	1233	42.8	3.5	8.0	5.2
8.	Saharpura Market	15-7-70	1258	34.9	—	7.0	6.5
9.	Rohraband	16-7-70	1461	27.7	0.5	6.5	7.5
10.	M. D. Bungalow	18-7-70	1510	51.5	—	7.5	6.8
11.	Main Hospital Area	23-7-70	1560	26.4	—	7.0	8.0
12.	Sindri Lake Area	24-7-70	1635	30.7	—	7.5	7.2
13.	Manohartan	25-7-70	1862	13.2	—	4.0	6.5
14.	Rangamatia	26-7-70	2038	26.3	—	7.0	4.8
15.	Sindri Farm Area	28-7-70	2113	18.7	—	4.5	8.0
16.	Domgarh Colony	29-7-70	2240	78.9	4.7	10.0	7.8
17.	Goshala (Moti Nagar)	1-8-70	2642	—	—	4.5	8.0
18.	B.I.T. Colony Area	2-8-70	2717	—	—	4.0	6.35
19.	Rangamatia (end)	4-8-70	2768	27.8	5.4	6.5	7.25
20.	Gamma Garden	6-8-70	2972	27.2	—	6.0	8.0
21.	NCA Poultry Farm	9-8-70	3622	14.0	—	4.0	6.5
22.	Sindri Pump House	10-8-70	4030	46.3	3.8	7.0	5.2

less than that of radon (Fig. 3). This is because radon decay products contribute much more to the atmospheric radioactivity in comparison to the thoron products because of their shorter half-lives and slower diffusion rate from soil to atmosphere. During sample collection, it has

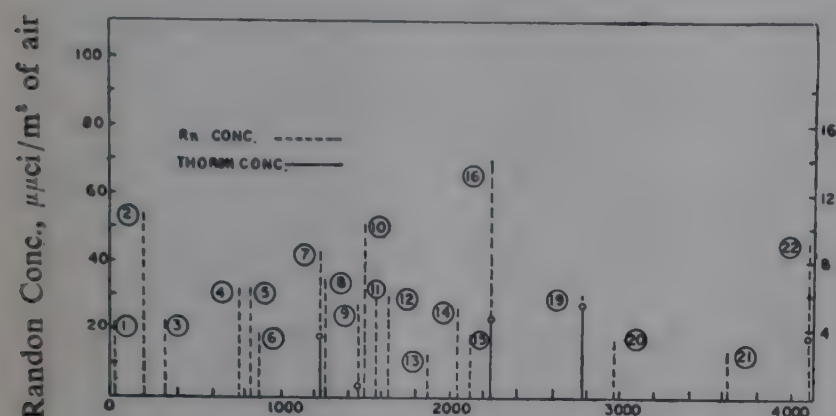


Fig. 3—Radon and Thoron Concentration at Different Sampling Points

been observed that the total β -activity as well as radon and thoron concentrations of the atmosphere decrease immediately after the rainfall; in fact, if the rainfall is heavy the atmospheric radioactivity is effectively limited to radon gas and its short-lived product RaA. In general, γ background of the locality was found more or less constant with the maximum dose-rate $8.0 \mu\text{r}/\text{hr}$ and may be attributed to natural sources. A random fluctuation in the activity of long-lived β -particles was also marked, which was due to the activity of fall-out particles from nuclear detonations. This type of random fluctuation in the fall-out activity near this area was observed earlier by one of the authors¹.

¹ Das, S. K., and Chatterjee, S. D., *Ind. J. Meteor and Geophys*, 15 (1964), 487.

EDITOR'S NOTE

TECHNOLOGY accepts research papers from scientists and technologists outside FCI Ltd., provided these are:

- (i) original and related to science and technology
- (ii) approved by external referees chosen by the Editor, and
- (iii) communicated from reputed institutions and written by workers with adequate experience.

Papers for publication in TECHNOLOGY are, therefore, welcome. These should be sent in duplicate (complete with illustrations and abstracts) to the Editor. Short communications, research notes, etc. are also accepted. Books, reports, proceedings of symposia, conferences, etc., meant for review in this journal, are welcome.

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Review

Proceedings of the Seminar on Application and Results with N-P Fertilizers, Particularly Nitrophosphates with Differing Citrate- Water-soluble Phosphate Contents [Technology Vol. 7 (1970), No. 2, Special Issue, 128 pp. Price Rs. 10/- or \$ 3.00]

The publication, viz. Proceedings of the seminar, held at the Planning and Development Division, FCI Ltd., Sindri, on December 18-19, 1967, contains 25 papers written by leading specialists on the subject from different parts of the country.

The report begins with a valuable introductory address of Dr. K. Ramiah, the then Vice-Chancellor, Orissa University of Agriculture and Technology, Bhubaneswar. He has stressed the necessity of adding complementary doses of nitrogen and phosphorus to crops. He has also dealt with the relative merits of the various N-P fertilizers. The relative efficiency of water-soluble and citrate-soluble phosphates is very important and from this point of view the publication is very timely. The general conclusion brought out by the papers is that while it is desirable to have certain percentage of the phosphate in the N-P fertilizers in the water-soluble form, nitrophosphate which contains phosphate fully in the citrate-soluble form is a very important phosphatic fertilizer. It is observed that the percentage of water-soluble phosphate needed in nitrophosphate depends on the crop and the soil. It has been

shown also that by suitable treatments, such as addition of organic matter, nitrophosphate which contains the whole of the phosphate in citrate-soluble form may profitably be used.

Some of the papers deal with the relative efficiency of ammonium and nitrate ions for rice. This subject is important for planning for N-P fertilizer production in the country. The publication ends with a thought-provoking article by Dr. K. R. Chakravorty on Planning for Phosphatic Production in India—A Perspective Approach, which has suggested the vital role which nitrophosphate is likely to play in our country in increasing crop production. The conclusions and recommendations of the Seminar are important.

There is no doubt that the report will be very useful to planners, technicians and extension workers dealing with the production and use of N-P fertilizers. The publication will be a valuable addition in the libraries of agricultural research institutes and of workers concerned with the development of agricultural science in general and of soil productivity in particular.

S. P. Raychaudhuri,

*Chief Agronomist, Shriram Khad Programme
[Formerly Senior Specialist (Land Resources),
Planning Commission]*

PROCEEDINGS OF THE SEMINAR ON COAL AND COAL CHEMICALS

The complete proceedings of the above seminar, held at Sindri in November 1968 under the joint auspices of the Calcutta Regional Centre of the Indian Institute of Chemical Engineers and the Coke Oven Managers' Association (Indian section), are to be printed as a Special Issue of TECHNOLOGY. The mss. is already in the press. This issue will also carry the First H. L. Roy Memorial Lecture delivered by Dr. K. R. Chakravorty, Managing Director FCI Ltd.

Notes & News

FCI's Coal-based Fertilizer Plant at Ramagundam

Dr. Triguna Sen, Union Minister of Petroleum & Chemicals, in laying the foundation stone of the Rs. 71 crores fertilizer plant at Ramagundam in Andhra Pradesh on October 2, stressed the need for greater cooperation among the FCI, Singareni collieries and the State Government. He particularly urged the collieries to take all steps to ensure that uniform quality of coal was maintained at all times. The factory would produce 3 lakhs tonnes ammonia, equivalent to about half-a-million tonnes of urea. Its location has been chosen as the plant's ultimate production could be consumed within a radius of 200 km in the land-locked Telangana region in preference to movement of fertilizer from coastal areas. The techno-economic projections indicate an anticipated return of 15 per cent on the capital employed, which will be paid back in 4 years. When commissioned, the factory would save annually

Rs. 36 crores in foreign exchange by way of reduction in fertilizer exports and another Rs. 120 crores by replacement of imported foodgrains. Despite heavy capital investment, including a foreign exchange component of about Rs. 20 crores, the cost of production would be competitive with any other more easily processable feedstock like naphtha.

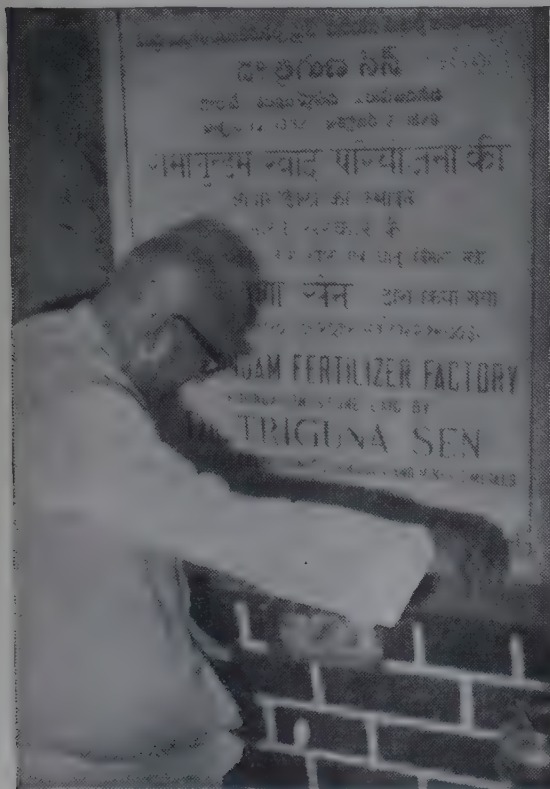
Sri Brahmananda Reddy, Chief Minister of Andhra Pradesh, wanted that FCI and the State Industries Department should work out methods to bring into existence a whole range of new enterprises, either by planning and setting up a large workshop designed to meet all the requirements of the fertilizer unit or by setting up a workshop only for its major needs and locating and selecting potential small entrepreneurs and technocrats willing to set up small ancillary units that could supply allover other items required by the fertilizer unit. This unit along with Pochampad irrigation project would change the face of Telangana region.

Dr. K. R. Chakravarty, Managing Director, FCI Ltd., stated that coals from the Ramagundam and Singareni collieries will be used as feedstock and for steam generation respectively. At normal levels of operation, the project shall require 0.8 million tonnes of coal annually, which even at an output/man shift (OMS) of 0.8 shall create additional employment to the extent of about 3500 workers in mining alone, besides providing employment to 200 skilled workers directly. Water would be drawn from river *Godavari* and power from the Ramagundam Thermal Station of the State Electricity Board.

The process is based on the gasification of coal licensed from Heinrich Kopper of W. Germany. Hydrogen sulphide and carbon dioxide removal steps are based on Rectisol process under license agreement with Lurgi of W. Germany. The ammonia synthesis and urea processes have been obtained by extension of process license agreements from Montecatini-Edison already being used in several projects of FCI. This plant will save Rs. 4 crores foreign exchange annually because of utilization of indigenous coal instead of importing naphtha.

Nuclear Power and Agro-Industrial Complex in India

While delivering the 31st Jagadish Chandra Bose Memorial Lecture on Nov. 30, 1969 at Calcutta, Dr. H. N. Sethna, Director, Bhabha Atomic Research Centre pointed out that cheap power at the cost of 1-2 paise per kWh can be economically used for the production of fertilizers. For the production of ammonia, which is the main form of fixed nitrogen for fertilizer, the present plants are based on naphtha or natural gas. With cheap electricity electrolysis could compete with these alternative processes. Figs. 1 and 2 give the comparison of the erected costs of urea plant and the cost of production of urea respectively. Similarly with sulphur prices increasing steadily, the use of electric furnaces for the



Dr. Triguna Sen, Union Minister of Petroleum & Chemicals, and Mines & Metals, laying the Foundation Stone of the Ramagundam Fertilizer Project on Oct. 2, 1970.

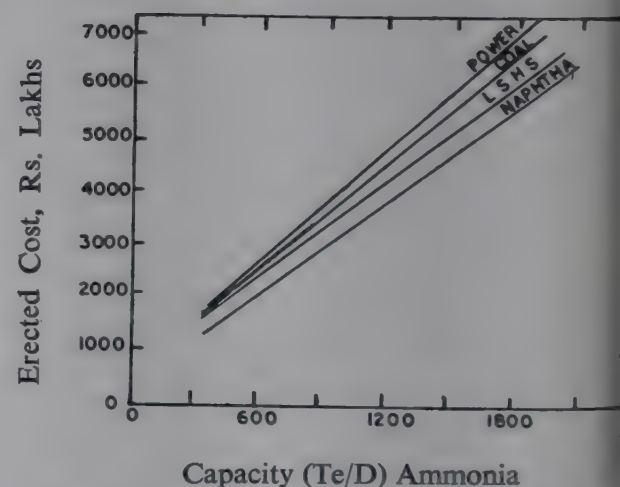


Fig. 1—Urea Plant Including Ammonia Plant

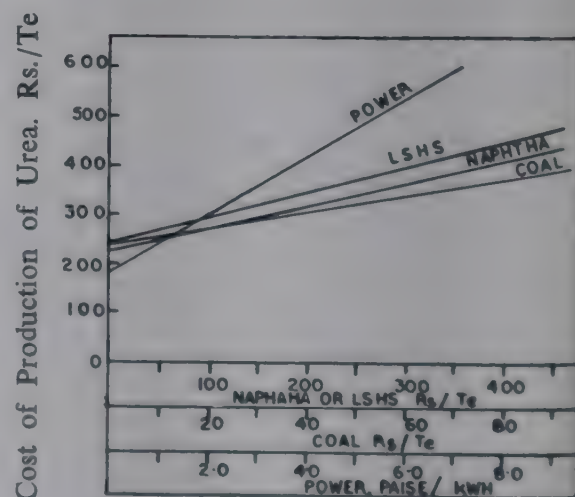


Fig. 2—Urea—Cost of Production

production of phosphorus for phosphatic fertilizers is assuming importance. Studies indicate that phosphatic fertilizers produced by the electro thermal process at a power cost of 2.6 paise per kWh can compete with the conventional process using sulphur at more than Rs. 485 per tonne.

The Government of India constituted a working group of scientists and engineers from the Bhabha Atomic Research Centre and representatives from official and non-official organizations to study the probable locations for such complexes and to analyse their economic implications. The study group has brought out interesting findings regarding the economic viability of agro-industrial complexes based on a nuclear power plant of about 1000-12000 MW in the Kutch-Saurashtra area and in the western Indo-Gangetic plain. In the Kutch-Saurashtra area a nuclear powered agro-industrial complex producing 470,000 tonnes per year fixed nitrogen and 331,000 tonnes per year P_2O_5 with 550,000 tonnes per year of aluminium and 150 million gallons water per day from a desalination plant would require an investment of Rs. 600 crores (Table 1) with a return on the investment on the industrial portion of about Rs. 71 crores. The desalted water would provide for additional food production of 600,000 tonnes which could meet the requirements of one million people. The income from the farm sector will be about Rs. 14 crores (Table 2). In the western Indo-Gangetic plain an investment of Rs. 430 crores (Table 3) would lead to the production of 636,000 tonnes per year of plant nutrient, 50,000 tonnes per year of aluminium and energise tube wells for ensuring irrigation of 720,000 hectares (Table 4). The income from the industrial portion is estimated at Rs. 57 crores and from the farm portion Rs. 213 crores. Such agro-industrial complexes producing cheap power can lead to overall prosperity of the nation and make significant contributions to the national economy freeing such complexes from the limitations on the size of the power station imposed by the size of the grid.

Phosphate Deposits of Rajasthan (India)

In March, 1966, some phosphorite occurrences were located at Birmania in Jaisalmar district, Rajasthan. The phosphorite band is traceable for a distance of about 4 metres trending in N-S direction from Birmania to Kohra. The thickness of the phosphate band varies considerably from

Investment Costs			
Plant	Capacity	Cost in Crores of Rupees	
		Foreign Exchange	Total
Dual purpose plant	1200 MWe 150 MGD	75.6	370.4
Fertilizers*	5330 Te/day	49.24	180.12
Ammonium Plant	150 Te-day	17.494	38.687
Total for Industrial Complex	—	142.334	598.207
*Ammonium Nitrate 3330 Te/day Diammonium Phosphate 1000 Te/day Triple superphosphate 1000 Te/day			

Agricultural Economics of the Project		
Area to be irrigated		
Triple cropping		9,200 hectares
Single cropping		38,400 hectares
Agricultural Production		
Hybrid maize		192,000 tonnes
Potato		390,000 tonnes
Groundnut		46,000 tonnes
Fertilizer Product		
Nitrogen as fixed N_2		447,000 tonnes
P_2O_5		331,000 tonnes
Fertilizer consumed in Complex		
Nitrogen as fixed N_2		3,900 tonnes
P_2O_5		3,100 tonnes
Net return of the project		Rs. 136.7 million

1 to 3 metres. The phosphatic materials have been found to occur either in association with the sandy calcareous layers or with cherty materials. The cherty phosphatic layer has a typical greyish blue shine. The phosphatic materials in some cases have been found to occur in the form of elliptical nodules or pellets of collophane embedded in sandy calcareous matrix. Free calcite, quartz are the common minerals

associated. The reserve of phosphate estimated in the area is of the order of about 4.34 million tonnes averaging about 10 per cent P_2O_5 down to depth of 10m along the dip. These include 3.64 million tonnes averaging about 10.22 per cent P_2O_5 in the Birmania block, 5, 53, 670 tonnes averaging 8.26 per cent P_2O_5 in the Kohra block and 1,46,000 tonnes averaging 9.27 per cent P_2O_5 in Ladhu Sing block.

TABLE 3—AGRO-INDUSTRIAL COMPLEX WESTERN INDO-GANGETIC REGION

Plant	Capacity	Investment Costs	
		Cost in Crores of Rupees	
		Foreign Exchange	Total
Nuclear Island Electric Plant	1200 MWe	31.600	158.000
Power Plant Total	—	13.400	67.000
Fertilizers*	1200 MWe	45.000	225.000
Aluminium Plant	4475 Te/day	44.911	166.283
Total of Industrial complex	150 Te/day	17.494	38.687
	—	107.405	429.970
*Ammonium Nitrate	3200 Te/day		
Dimmonium Phosphate	1275 Te/day		

TABLE 4—AGRO-INDUSTRIAL COMPLEX INDO-GANGETIC PLAIN

Agricultural Economics of the Project		
Area to be irrigated (Hectares)		720,000
Number of tubewells		36,000
Products (additional) in tonnes		
General		4.5 million
Pulses		0.7 million
Net return of the Project	Rs. 2512	million
Fertilizer requirements (in tonnes)		
Nitrogen as fixed N ₂		166,000
P ₂ O ₅		83,000
Total investment on drilling	Rs. 432	million
Net return per hectare	Rs. 3767	

(Sci. and Cult., 36 (1) (1970), 5)

The another deposit was discovered in April 1967, about 88 km north of Barmer near Fatehgarh by the side of Jaisalmar-Barmer road. It comprises essentially coarse gritty ferruginous phosphatic sandstone with interbedded clays. Included within the sandstones are phosphatic colites and pellets. Besides these sandstones contain fossil remains like coprolite, gastropods, oastro-cods, and tamellibranchs. Numerous fragments of bones of various shapes have also been observed in slides. Many bones have been replaced by collophane and later by calcite. Glauconite, magnetite, zircon, tourmaline and cherts occur as accessories.

Samples collected from different parts of the deposit have indicated P₂O₅ varying from 5 to 15 per cent. It is, however, felt that average grade of the material may contain only about 8 per cent P₂O₅. Reserves are not yet estimated but they are likely to be large.

Three deposits of phosphate were discovered in Kanpur area of Udaipur district in March, 1967. They are at Kanpur, Maton and Karbaria-Ka-Gurha. Kanpur deposit occurs about ½ km south of Kanpur in an undulatory topography. It is associated with dolomite and cherty quartzite. A large number of samples collected from

these outcrops on analysis have indicated that the percentage of P₂O₅ varies from 10 to 25, although the algal-bearing samples sometimes have given upto 35 per cent P₂O₅. It is hoped that the average grade of material would analyse about 15 per cent P₂O₅. The likely reserve of deposit is 2.1 million tonnes. Maton block deposit is located about 3-4 km east of Kanpur near the village Maton. The phosphorite horizon shows great variation in thickness right from one metre to 20 metres. The horizon within the cherty quartzite is thicker than seen in dolomite and quality of phosphorite is comparatively better. A large number of samples collected from the different parts of the Maton deposit on analyses gave 20 to 30 per cent P₂O₅. Reserves are estimated at 5 million tonnes. At Karbaria-Ka-Gurha phosphorite occurs on small billock extending in NE-SW direction for a distance of about 1.5 km. The phosphatic material is associated with dark grey cherty quartzite, dolomite. The phosphorite horizon, however, is not traceable continuously and appears to be of pinching and swelling type. Samples on analysis showed P₂O₅ varying from 10-20 per cent. The reserves are estimated at 0.6 million tonnes.

The occurrence of phosphorite near Dakan Kotra, about 12 km S-N-E of Udaipur was discovered in May 1967. The nature of occurrence is very similar to that seen at Maton and Kanpur. Samples from this locality on field analysis have indicated the P₂O₅ per cent varying from 10-20. Another occurrence of phosphorite is just to the west of Dakan Kotra, on a small hillock about 30 m. high. It is traceable for a distance of about 400 m along the strike. The material is associated with cherty quartzite in the southern portion and with dolomite in the northern portion. The reserves of Dakan Kotra are estimated at 2 million tonnes.

Phosphate deposit in Sisarma area, Udaipur district is located about 5 km south of Udaipur. The horizon varies from 4 to 5 m in thickness and is reported to extend impersistently over a strike length of about 4-5 km. The phosphate bands analyse between 10 to 15 per cent P₂O₅ rarely showing 20 per cent. But the average grade of material from the entire phosphorite horizon may not analyse more than 10 per cent. The phosphate deposit in the Newania area, Udaipur district is located about 45 km east of Udaipur. There are apatite veins in a coarse crystalline carbonate rock extending in an area of about 3 Sq. Km. The individual apatite veins vary in the

thickness from 5 mm to 20 cm and extend upto a maximum of 20 m. Results of bulk samples from all over the exposure and core samples (based on one hole only) show 6 to 10 per cent P_2O_5 content. The reserves of both Sisarma and Newania are to be estimated yet.

The Jhamar Kotra deposit is located about 28 km. south-east of Udaipur city. The phosphate rock bed is traceable for about 16 km in the NW-SE direction. Two varieties of phosphate rock have been noticed in this area—one with abundant carbonate and the other with low carbonate. A preliminary estimate of reserve upto 30 metres depth in blocks A, B, C and E are 8.10, 3.96, 6.60, and 7.20 million tonnes respectively. Assay value of phosphate rock samples show P_2O_5 content something ranging from 16 to 37 per cent. 'D' block representing about 1,600 metres of strike length has indicated quality of 30 per cent and above of P_2O_5 and reserve about 11 million tonnes.

In the absence of surface investigation by drilling, it is premature to indicate the reserves of phosphorite in the deposit. However, assuming that the phosphate horizons as met within the different deposits would maintain by and large their grade and thickness in depth it may stand to reason to visualise the reserves in the individual deposits as already stated.

Regarding commercial exploitation of Rajasthan rock phosphate Birmania phosphate deposit is beset with several difficulties as regards mining and exploitation. The deposit is of low grade. The gangue material is hard chert and lime which would create difficulties in beneficiation. Direct application of the material in powdered form also does not appear to be possible owing to the injurious effects of large quantities of lime associated with collophane. The deposit is exploitable mostly by underground mining and due to the thinness of phosphate horizon the mining may be costly. The deposit is located in an inaccessible sand dune country and the road transport will be difficult and expensive. The nearest railhead is 120 km and the cost of transport by road will be prohibitive. Water is scarce in the area which may create difficulties in beneficiation even if the material is found amenable for the same. Labour in the area is also not in plentiful and has to be obtained from outside. As there is not much lime associated with the Fatehgarh rock, beneficiation may be relatively easy.

A bulk sample from the part of the

Kanpur deposit sent to National Metallurgical Laboratory, Jamshedpur for beneficiation test showed the material to contain 35-40 per cent P_2O_5 . Of all the deposits discovered so far in Udaipur district, the Maton deposit appears to be the best. As the phosphorite bands occur in a hill rising about 100 m. from the surface it may easily be worked by quarrying for some distance and later by under ground mining.

(*Indian Minerals*, 21 (2) (1967), 83 and *Fertil. News*, 14 (9) (1969), 44)

Potassium from Sea-Water

About 40,000 tonnes of potassium chloride can be manufactured annually on the basis of practical recovery from sea water bittern, the only source of potassium in India. Studies were undertaken at the Central Salt & Marine Chemicals Research Institute, Bhavnagar on the recovery of potassium chemicals in the following lines: (1) recovery of mixed salt, a fraction containing 18-20 per cent potassium chloride by the solar evaporation of bitterns; (2) utilization of mixed salt to obtain potassium chloride and potash alum; and (3) recovery of potassium chemicals directly from sea water and bitterns using dipicrylamine as selective precipitating agent. Laboratory studies were extended to field scale trials successfully in harvesting mixed salt in solar salt works. Pilot plant studies were carried out to collect the required data and to find out the economic feasibility of the process developed for the manufacture of (i) potassium chloride along with magnesium sulphate and sodium sulphate and (ii) potash alum.

Addition of 36°Be bittern to 29°Be bittern has been found to effect 70-80 per cent separation of potassium chloride as mixed salt at lower densities (34-36°Be). Also, the addition of required quantities of $MgCl_2$ and Solivan Green was found to reduce the period of evaporation from 20 to 9 days to obtain 36°Be bittern stage.

A novel process of hot extraction of mixed salt using 36°Be by-product bittern to obtain potassium chloride in the presence of large amounts of magnesium sulphate has been worked out. In this process it is possible (i) to obtain potassium chloride from mixed salt without desulphatation or addition of any other chemicals; (ii) to recover the by-products, viz. epsom salt and sodium sulphate which make the recovery of potassium chloride economically feasible. Based on this process, a commercial pilot plant of producing 3 tonnes of potassium

chloride and 7 tonnes of epsom salt per day has been set up at Kandla.

The second process developed for obtaining potash alum from mixed salt is simple and suitable for small scale salt works. The process consists in adding mixed salt to 35 per cent aluminium sulphate (ferric alumina grade B) solution heated to 110°C and filtering hot to crystallize pure alum. The entire potassium chloride of mixed salt is converted to potassium sulphate at the expense of magnesium sulphate, which is also present in the mixed salt, and is recovered as potash alum of pharmaceutical grade. A tonne of mixed salt and 0.46 tonne of aluminium sulphate yield 1.2 tonnes of potash alum. The process has the following advantages: (i) it is cheaper than the conventional process of manufacture of potash alum; (2) recovery of potassium from mixed salt is over 90 per cent; (3) it is suitable for cottage-scale industries; (4) only inexpensive equipment as are available in the country are required; and (5) the price obtained per unit K_2O alum is high.

The recovery of potassium ions at room temperature either as potassium nitrate or potassium sulphate direct from sea-water and bitterns using dipicrylamine (calcium salt) as precipitant has been investigated. It was observed that recoveries of potassium salt from sea-water and 29°Be bitterns are 78 and 92 per cent respectively.

[*CSIR News*, 20 (19) (1970), 146]

Arzew (Algeria) Complex Comes On-Stream

The discovery of natural gas deposits in Hassi R'Mel, led to the setting up of the large nitrogen fertilizer complex, at Arzew, by Sonatrach, the state-owned oil and gas concern.

First conceived in 1965, this complex was a considerable undertaking in that not only are the fertilizer production units relatively large for a country, such as Algeria, hitherto little industrialized, but all off-site installations, including facilities for shipping ammonia and finished fertilizers also, had to be created from a virtually unprepared coastal site. Steam, electric power, compressed air, sea-water intake and sea-water desalting units, in addition to offices, laboratories, a restaurant, stores and workshops, all had to be erected before efficient operation of the actual plant could begin.

The individual production units consist of a natural gas reforming furnace fed by gas brought by a pipeline from Hassi

R'Mel, some 300 miles to the south-east, a 1,000 t.p.d. ammonia converter, a 400 t.p.d. nitric acid (100%) unit, a 500 t.p.d. ammonium nitrate facility and a 400 t.p.d. urea plant; the finished complex was ready to start production exactly on schedule in March 1969, some 30 months after process studies commenced.

In competition with a number of construction firms, the Cie Francaise d'Etudes et de Construction (TECHNIP) and ENSA SA, [formed by Schneider Creusot and Cie des Ateliers et Forges de la Loire (CAFL)], were jointly awarded the turnkey contract, valued at around \$ 50 million, in July 1966. The Chemical Construction Co. (Chemico) began process studies in September 1966, and twelve months later the foundation stone of the complex was laid down. At the time a further contract was signed between Sonatrach and the TECHNIP/ENSA group for the hiring and training of a large number of engineers, technicians and other specialists responsible for the operation of the plant. Eighty qualified specialists were placed at Sonatrach's disposal for the start-up and running of the various units, until Algerian personnel are ready to take over, following training arranged in collaboration with the Algerian Petroleum Institute, together with long training periods at TECHNIP for engineers and technicians.

Chemico processes have been used throughout the units, which are all single-train and which include two circular prilling towers for ammonium nitrate and urea respectively. The size of the 1,000 t.p.d. ammonia section necessitated special arrangements for delivery for some of its components, such as the impressive ammonia converter and the flash tower, in which carbon dioxide in the exit gases from the natural gas reforming section is fixed and separated from the amines, before being conveyed to the urea plant. Because of its unusual size the flash tower (height 150 ft. diam. 163 in.) was lowered into the water, towed to the beach, and then placed on specially-designed tractor units, while even more elaborate measures were necessary for landing the converter, which weighed around 400 tonnes. A large barge was used to ship the converter to a purpose built quay at Arzew, from where it was transported on the undercarriage of a large transport plane, towed by a 100-tonne crane.

The bagging and storage houses for the ammonium nitrate and urea occupy a surface area of 7.5 acres, and comprise a

10,000 tonne bulk urea store, an automatic bagging shop, and warehouses for bagged ammonium nitrate and 15,000 tonnes of bagged urea. There are also facilities for storing ammonia at a low temperature, before being conveyed by a two-mile long pipeline to Arzew harbour, where it is fed into a 20,000-tonne refrigerated tank, maintained at -28°F (-33°C). Ammonia tankers will be loaded from this tank at a rate of 52,000 ft.³ p.h.

(*Nitrogen*, No. 63 (1979), 16)

New Ammonia Plant in Finland

A new ammonia plant of 825 stpd capacity has gone on stream at Oulu (Finland), which is the second plant to use centrifugal gas compressor at the full economic conversion pressure of 300 atm. Its feature is that it is the first to combine 300 atm centrifugal synthesis gas compressors with the simplified ammonia synthesis loop using ICI's quench converter, showing useful savings in both capital and utilities when compared to the previously common lower synthesis pressure designs.

Feedstock naphtha, after bulk sulphur removal in a hydrosulphurization unit, is vaporized in a fired heater, and the last traces of sulphur removed across a bed of zinc oxide. It is then mixed with a controlled amount of steam, superheated in the convection section of the primary reformer and then fed to the primary reformer tubes at 480°C and 34 atm. Reformed gas leaves the tubes at 820°C . Process air, compressed by centrifugal compressor to 32 atm and superheated to 560°C is fed to the secondary reformer, in which the methane content of the reformed gas stream is lowered to about 0.2 per cent. Exit gases are immediately cooled by heat exchange and further cooled in steam superheaters and in a methanator feed preheater.

Conversion of carbon monoxide to carbon dioxide is carried out in 2 stages—first at high temperature with 370°C inlet, and the second at low temperature with 215°C inlet. The carbon monoxide shift effluent gas is cooled and fed to the carbon dioxide removal section in which the carbon dioxide is removed from synthesis gas by an activated potassium carbonate solution. The carbon dioxide-free gas is reheated to 350°C and the residual carbon oxides catalytically converted to methane.

The purified synthesis gas is then compressed in the four barrel Nuovo Pignone centrifugal compressor which discharges at 300 atm. The fresh make-up gas is mixed

with recirculating gas from the converter and passed to the inlet of the quench converter. Part of the gas stream is passed directly to the converter after heat exchange with the converter effluent and the remaining gas is used as quench gas. After reaction the converter effluent is cooled by heat exchange with the incoming reactants and by boiler feed water preheating, the remaining heat being dissipated in air and water coolers. Product ammonia is condensed out in these coolers, separated from the gas stream and passed to battery limit. Ammonia is recovered from the purge flash gases by water absorption.

Steam is generated at 120 atm to provide power for turbine drive of the synthesis gas compressor which passes out at 400 atm to the reformer and is back-pressured at 4 atm to provide steam for plant heating and export requirements. The process air compressor turbine is a condensing machine driven by 40 atm steam.

The synthesis loop was designed to operate at 300 atm because it gave the following advantages: (i) it increases reliability and ease of operation, (ii) minimizes capital and production costs.

Compared with lower pressure operation, the increase in synthesis gas compressor cost is more than off-set by the decrease in refrigeration compressor and related equipment costs. The decrease in refrigeration and recycle power again favour the higher pressure operation, and this is naturally reflected in lower operating cost. Quench converter was selected because it led to minimum investment and maximum ease of maintenance.

(*Nitrogen*, No. 62 (1970), 21)

Hungarian Nitrogen Industry

The last 8 years have seen an almost 5-fold increase in the output of nitrogen in Hungary, where capacity is in existence to produce a significantly greater amount than the 253,000 tonnes N₂, which originated from Hungarian chemical complexes during 1968. As in the majority of the East European countries, Hungary had an almost wholly agricultural economy until after the World War II, when a significant proportion of what heavy industry the country did possess was destroyed either by Allied air attacks and shellings or by the retreating German forces. During the post-war years a high proportion of annual investment was channelled into the industrial sector of the economy, with the chemical industry representing one of the major recipients.

This industry was established in 1932 the first synthetic ammonia plant was started at Varjalsota based on a indigenous lignite gasification process. Initially manufacturing CAN (15.5 per cent N) output ranging between 679 and 6432 tes N (1932 to 1937), it was expanded in 1938 to 40 tpd ammonia. During the war it was operated at a high utilization rate until bombed by the Allies in 1944/45. It was restarted in 1946 but full production started until the end of that decade when the main end-product continued to remain CAN (20.5 per cent N). A further expansion was completed in 1956, bringing the capacity to around 33,000 t N/yr, when the nutrient content was upgraded to 25 per cent N. A fourth expansion completed in 1968 not only increased the production capacity of the existing product but also increasing the range of fertilizers available including urea. A new, natural gas-based 420 tpd steam-reforming ammonia came into operation by the end of 1969, accompanied by expansions to the acid and nitrates plant as well as by the opening a new urea unit of 100,000 tpa capacity.

The late-1950 saw the growth of a second nitrogen complex at Kazincbarcika based mainly on natural gas, being converted from coke oven gas in 1964, as opposed to the lignite based plant at Varpalota. Hungarian nitrogen industry is based almost wholly on domestic sources of gas and a significant network of oil and natural gas pipelines has been built up. By 1975 the supply of natural gas is expected to reach some 6,500 mil.cu.ft./yr of which some 1000 cu ft will be imported mostly from USSR through an extension of the existing line from Soviet Union to Czechoslovakia. The use of natural gas brought significant economies in the production costs for ammonia—whereas from solid fuel at Varpalota its cost is florints 9500 the natural gas-based is F 7000/te of nitrogen. By July 1966 the range of products at Kazincbarcika in addition to CAN has been extended by the addition of a 5000 te/yr caprolactam unit with a co-product ammonium sulphate capacity of about 30,000 te/yr., while at the same time a replacement of the ammonia plant, of 450 tpd capacity, was also completed.

As part of the trend in Europe, a urea unit of 300 tpd capacity came on stream in mid-1967. Constructed with Soviet aid and equipment this plant at Tiszapalkonya centred around a number of small natural gas-based ammonia units totalling some 82,300 tN/yr. Nitrogen production during 1968 was as follows: ammonium sulphate

7000 te, urea 50,000 and ammonium nitrates 195,000 tonnes.

[*Nitrogen*, No. 63, (1970), 24]

Safety in Fertilizers

In a paper read at the first national conference on industrial safety organized by the National Safety Council Bombay, P. S. Kukillya, Chief Inspector of Safety, Fertilizer and Chemicals Travancore Ltd., dealt with some of the hazards in fertilizer industry. Chemical hazards fall into the following broad divisions due to: (i) fire or explosion and (ii) chemical action on materials of construction or on human tissues. Preventions against certain raw materials, products, etc. used in the manufacture are given below:

Naphtha: Highly volatile, it can form an explosion mixture with a lower limit of 0.9 per cent and an upper limit of 6 per cent. It can cause dermatitis.

Where naphtha handling equipments are in confined areas, there should be effective arrangements for the removal of naphtha vapours. There should be adequate ventilation and only explosion-proof electric motors and equipment should be used. Pumps and pipelines handling naphtha should be effectively grounded to prevent accumulation of static electricity. Before allowing any person to enter vessels which might have contained naphtha, it should be thoroughly purged preferably by using steam.

Hydrogen: It is highly explosive when mixed with air or oxygen. The following are the explosive limits:

	Lower limit %	Upper limit %
Hydrogen in oxygen	4	94
Hydrogen in air	4	74

Only explosion-proof motors and equipments should be used. To prevent formation of explosive mixtures good ventilation should be ensured. Where it is necessary to repair any vessel or pipeline carrying hydrogen or a mixture containing hydrogen, it should be thoroughly purged by nitrogen or an inter gas.

Ammonia: When stored in a closed container, liquid ammonia exerts a vapour pressure which increases rapidly with rising temperature. Ammonia will form an ex-

plosive mixture with air or oxygen. A mixture of ammonia in air of concentrations 15 and 25 per cent by volume is inflammable and explosive. Exposure to a heavy release of this gas may injure cornea and cause blindness, pulmonary edema. Chronic conjunctivitis and bronchitis may also occur from prolonged exposure.

Never use an open flame to test leaks. Determine its exact location by passing a slightly open test cylinder of liquid sulphur dioxide or hydrochloric acid near all joints and watch for fumes when the leak is located. Good ventilation specially at the upper parts of the building should be ensured. The rules applicable to the filling of gas cylinders with liquid ammonia should be strictly followed. Ammonia lines should be laid above ground or in ventilated trenches. Aluminium or copper gaskets should not be used; mild steel, pure nickel or lead gaskets are suitable.

Carbon Monoxide: It is a colourless, odourless and flammable gas. Its explosive limit by volume in air is 12.5 to 74.2 per cent. It can damage brain and cause heart disease; very severe dose can cause coma.

Adequate ventilation should be provided near carbon monoxide and every workmen should wear a breathing apparatus. Its concentration in the atmosphere should never exceed 100 parts/mil. parts for an 8 hours' exposure and 400 parts/mil parts for 1 hr. in an atmosphere containing at least 19 per cent oxygen.

Phosphoric Acid: It is a corrosive acid causing burns. Care should be taken, when handling it, by wearing protective equipments, such as rubber shoes and gloves, gas-tight goggles.

Patents*

Phosphoric Acid: by L. W. Cochran (to Multi-Minerals Ltd.) U.S. 3,494,735, Feb. 10, 1970, Appl. July 31, 1964; 4 pp. (see Belg. 657,240, Apr. 15, 1965).

Apatite is digested with H_3PO_4 to prepare $Ca(H_2PO_4)_2 \cdot H_2O$ which is then treated with ion-exchange resin to obtain pure H_3PO_4 . For example, an acid leaching solution consisting of 96.0 g 85.6% H_3PO_4 and 53.5 g H_2O was heated to 90° in an open vessel. To the hot leaching medium was added 10 g apatite which had been pre-

*These patents have been reproduced from *Fertilizer Abstracts*, published by the National Fertilizer Development Centre, TVA Muscle Shoals, Alabama (USA) with kind permission of Editor, FA.—Editor

heated to 90°. The apatite contained P_2O_5 39.60, CaO 50.80, F 2.72, HCl soluble Fe 1.75, S. 0.57, SiO_2 4.34, Al_2O_3 0.08, and MgO 0.18%. The reaction was continued for 30 minutes at 90-100°. The resulting liquor was filtered through a hot Buchner funnel to remove insolubles. Upon cooling, $Ca(H_2PO_4)_2 \cdot H_2O$ crystallized from the filtrate. The crystalline product was separated by filtration, dried and weighed. The yield was 13.4 g and the insolubles weighed 0.52 g. The crystals were treated with a cation-exchange resin such as Amberlite IR-120 to produce pure H_3PO_4 .

(*Fertilizer Abstracts*, 3 (5) (1970), 99)

Removing Iron from Phosphoric Acid: A. M. Baniel, Ruth Blumberg (to Kaiser Aluminum and Chemical Corp.) U.S. 3,497,330, Feb. 24, 1970, Appl. Feb. 8, 1965; 4 pp.

Substantially Fe-free H_3PO_4 is prepared by treating phosphate rock with aqueous HCl and extracting the solution with iso-amyl alcohol (I) which selectively dissolves the Fe. Admixture of nitrobenzene (II) with I inhibits extraction of H_3PO_4 by the alcohol. Thus, a solution containing P_2O_5 104, HCl 61.5, H_2O 830, $CaCl_2$ 290, and Fe 4.0 g/liter was extracted with I in a counter-current system using 1 volume 1/5-10 volumes solution. The extracted aqueous phase contained P_2O_5 100, HCl 53, H_2O 830, $CaCl_2$ 330, and Fe 0.07 g/liter; the organic phase contained P_2O_5 40.7, HCl 50, H_2O 90, $CaCl_2$ 1.7 and Fe 17.6 g/liter. In a similar test using a mixture of I and II (mole ratio 1:1) the organic phase contained P_2O_5 10.2, and Fe 31.0 g/liter and the aqueous phase contained P_2O_5 102, and Fe 0.19 g/liter. Other suitable solvents include hexanol and amyl acetate.

(*ibid*)

Alkali Metal Phosphates: by Bryan Milling (to Electric Reduction Co. of Canada, Ltd.). U.S. 3,493,336, Feb. 3, 1970, Appl. Brit. June 18, 1964; 2pp.

Crude wet-process H_3PO_4 from the gypsum filter is mixed with sufficient Na_2SiF_6 to provide at least 7% Na_2SiF_6 in the reaction mixture. Then a Na salt such as Na_3PO_4 or NaCl is added to the mixture, whereby the F is precipitated as Na_2SiF_6 in not less than 30 minutes. The mixture is then filtered to obtain Na_2SiF_6 of good quality and color. The filtrate is mixed with synthetic FeS , Fe_2S_3 , or FeS_2 in an amount equivalent to about 0.15% of the P_2O_5 , neutralized with Na_2CO_3 , and filtered to remove precipitated metal impurities and unreacted sulfide. The

filtrate is then treated by usual methods to prepare Na phosphate of high purity.

(*ibid*, 100)

Production of Potassium Nitrate: by Oesterreichische Stickstoffwerke A. G. Austriam 227,284, Dec. 29, 1969, Appl. Oct. 27, 1967; 5 pp.; CA 72,45607.

In process for the manufacture of KNO_3 , by dissolving KCl in diluted HNO_3 at elevated temperatures, cooling the solution, collecting the solid KNO_3 , and recycling the mother liquor after removal of the formed HCl, the mixture is cooled after dissolving KCl to 25° and the precipitated KNO_3 is isolated while in the mother liquor which contains KNO_3 in addition to HCl and HNO_3 , the HCl is made to react with liquid or gaseous N_2O_4 with the formation of NOCl, and the HNO_3 formed is recycled to the dissolution process.

(*ibid*, 102)

Potassium Values from Sea Water: by C. L. Thomas (to Sun Oil Co.). U.S. 3,497,314, Feb. 24, 1970, Appl. Apr. 24, 1967; 2pp.

Natural glauconite (I) containing 5-10% K is treated with aqueous NH_4Cl solution which dissolves a portion of K. The treated I is then contacted with sea water whereby the K is selectively absorbed. The I is again treated with aqueous NH_4Cl to remove the K, and the cycle is repeated. Thus, finely ground I containing 8% K was stirred for two hours at 195°F. with 6N NH_4Cl solution. The eluant contained 1.1%K corresponding to 13.7% of the K originally present in the I. The treated I was then stirred at 70°F. with 10 volumes sea water containing 338 ppm K. The I was again treated at 195°F. with 6N NH_4Cl . The eluant contained 3% K. The cycle was repeated 10 times; the K recovered was 133.7% of that originally present in the I.

(*ibid*)

Phosphoric Acid: by R. M. O. Maunsell (to Electric Reduction Co. of Canada, Ltd.). U.S. 3,499,729, Mar. 10, 1970, Brit. Appl. Sept. 27, 1966; 4 pp.

In processing phosphoric acid according to the method of U.S. 3,404,954 (FA 1, 1710), wet-process H_3PO_4 is heated in submerged combustion evaporator to volatilize P_2O_5 and form an aerosol. The aerosol is cooled sufficiently to condense H_3PO_4 but not sufficiently to condense volatile impurities. In the present method, solid impurities that collect in the evaporator are continuously

withdrawn and separated by sedimentation in a vessel supplied with feed acid.

(*Fertilizer Abstracts*, 3 (6) (1970), 125)

Phosphoric Acid: by Robert Amanrich and Gilbert Cousserans (to Office National Industriel de l'Azote). U.S. 3,497,329, Feb. 24, 1970, Fr. Appl. July 5, 1966; 6 pp.

A process for producing high-purity H_3PO_4 from HNO_3 and phosphate rock consists of crystallizing $Ca(NO_3)_2$ from the digestion solution in two successive stages, liquid-liquid extraction of the mother liquor with an alcohol to dissolve the H_3PO_4 and HNO_3 from the aqueous phase, distilling off the alcohol, and treating the impure H_3PO_4 by liquid-liquid extraction with an ester which selectively dissolves the HNO_3 and leaves high-purity H_3PO_4 . The $Ca(NO_3)_2$ crystallizations are carried out at 0 to 10° and then at -5 to -15°. Typical composition of the mother liquor is H_3PO_4 49.8, HNO_3 3.2, and $Ca(NO_3)_2$ 8.0%. This is extracted with an alcohol, typically a solution containing 72% tertiary amyl alcohol in 27% water to give, after distilling off the alcohol, an aqueous solution containing 36.5% H_3PO_4 and 4% HNO_3 . Such product is suitable for direct use in preparing fertilizer solution is extracted with butyl acetate which selectively dissolves the HNO_3 . A typical composition of the aqueous phase from the butyl acetate extraction is 39% H_3PO_4 and 0.9% butyl acetate. After concentration to 55% H_3PO_4 the product contains typically HNO_3 0.05, CaO 0.075, MgO 0.004, and F 0.065% with indeterminable amounts of Fe, Al, and SO_3 .

(*ibid*)

Phosphoric Acid: by M. M. Striplin and F.P. Achorn (To Tennessee Valley Authority). U.S. 3,507,614, Apr. 21, 1970, Appl. Mar. 14, 1966; 8 pp.

In the usual process for making phosphoric acid by the furnace process, P is burned in air and the combustion products are reacted with water. In the process described, the water is supplied in the form of crude, dilute, wet-process phosphoric acid made in the usual way by treating phosphate rock with an acid. The wet-process acid is preheated by heat exchange with the combustion products, thereby driving off F and some of the water. The operation is carried out under conditions which result in the formation of pyro—and higher acyclic polyphosphoric acids, thereby sequestering

nonvolatile impurities from the wet-process acid.

(*ibid*, 126)

Ammonium Polyphosphates of Controlled Solubility: by C. Y. Shen and N. E. Stahlheber. U.S. 3,495,937, Feb. 17, 1970, Appl. Mar. 16, 1965; 6 pp.

The water solubility of ammonium polyphosphates can be controlled by heating in an atmosphere controlled in NH_3 and H_2O vapor content. Thus, a substantially water-insoluble ammonium polyphosphate was charged to an oven and heater to 250° in an atmosphere in which the NH_3 vapor pressure was 50 mm Hg and the H_2O vapor pressure was 710 mm Hg for about two hrs. The product had a high water solubility. Similarly, an ammonium polyphosphate of high water-solubility was mixed with urea and $\text{NH}_4\text{H}_2\text{PO}_4$ and the mixture was heated at 275° for 20 hrs in an atmosphere containing NH_3 vapor pressure of 475 mm Hg and an inert gas (for example, CO_2) vapor pressure of 274 mm Hg. The product was virtually insoluble in water.

(*ibid*, 129)

Pelletized Potassium Chloride-Urea-Sulfur Fertilizer: by P. E. Titus (to Shell Oil Co.). U.S. 3,501,282, Mar. 17, 1970, Appl. Sept. 9, 1966; 4 pp.

An agglomerated mixture of fine KCl, S, and urea is dried and the resulting pellets are briefly heated to provide a urea-S glaze on the surface of the pellets. For example, a mixture of sylvite 49.4, S 25, urea 25, $(\text{NH}_4)_2\text{HPO}_4$ 0.1, and oil 0.5% (the oil being entrained residue from pipeline transportation of an oil-sylvite slurry) was moistened with KCl brine and pelletized on a rotating sieve. The pellets were dried at $\sim 240^\circ\text{F}$ for ~ 17 hr and then glazed by an open flame for ~ 1 min. The pellets had a bulk density of 0.69 g/ml, were harder than pellets made from sylvite alone, and had a slower rate of dissolution in water.

(*ibid*, 130)

Granular Diammonium Phosphate: by P. B. Mischel and J. W. Patrick (to Petrochemicals Company, Inc.). U.S. 3,485,580, Dec. 23, 1969, Appl. May 12, 1967; 3 pp.

A modified process for the production of diammonium phosphate (DAP) which has substantially less tendency to cake than conventionally produced DAP, is described. Granulation of the title product is carried out according to conventional methods with an alkylaryl sulfonic acid or an alkali

metal salt of an alkylaryl sulfonic acid introduced in the reaction mixture. The alkyl radical containing 1-18 carbon atoms is added at a rate of 0.005-0.05 wt % of DAP produced. The use of larger amounts does not result in reduced caking and excessive amounts $>0.3\%$ may increase caking. In an example, a control cake of DAP without the alkyl radical was assigned a caking index of 100%; when 0.04% 1,2 dimethyl naphthalene sodium sulfonate was added a caking index of 30-50% was achieved in the cakes. The anticaking effect persisted in bulk or bag materials for several months.

(*ibid*, 131)

Slow-Release Fertilizer: by R. U. Schenk. U.S. 3,502,458, Mar. 24, 1970, Appl. Feb. 28, 1967; 10 pp.

A slow-release fertilizer is made by mixing a fertilizer material, a fibrous organic material, and a binder together, and heating at a temperature up to 380°F . and 100-8000 psi. The organic material preferably should make up about 10% of the mixture and the binder 3%. Organic materials such as sawdust or peat moss are suitable. Both thermosetting (for example, urea-HCHO) and thermoplastic (for example, polyolefin resin) binders can be used.

(*ibid*)

Method for Determining the Effectiveness of Anti-Caking Agent: by James Passmore (to Petrochemicals Company, Inc.). U.S. 3,481,187, Dec. 2, 1969, Appl. Dec. 19, 1966; 3 pp.

An apparatus for the determination of effectiveness of an anti-caking agent is described. Test results of the penetrometer to accurately predict the anti-caking results when a predetermined quantity of agent is added are given. Samples of materials containing various amounts of agents are subjected to pressure, using the hydraulic Carver laboratory press. The maximum pressure of the material in storage is normally the pressure used in the test. The samples are placed in a storage area at ambient temperatures and left for seven days. The penetrometer is then used to determine the force necessary to penetrate the caked portion of each sample. This is an indication of the degree of caking that takes place commercially.

(*ibid*, 132)

Improved Fertilizer Granules: by P. E. Titus (to Shell Oil Co.). U.S. 3,501,282, Mar. 17, 1970, Appl. Sept. 9, 1966; 4 pp.

Potassium chloride (I), with or without other fertilizer materials, is first granulated by mixing with S and urea, wetting, granulating, and drying. The granules are then heated to melt the S and urea on the surface, thereby glazing the granule and giving it high strength. The S urea wt ratio should be between 1:2 and 2:1; the finished granules should contain at least 35% of finely ground I and 5-40% of the S-urea mixture.

(*ibid*, 132)

Sodium Bicarbonate and Fertilizer Salts: by Hideo Arita (to Asahi Kasei Kogyo Kabushiki Kaisha). U.S. 3,506,432, Apr. 14, 1970, Japan Appl. Apr. 28, 1965; 3 pp.

A process is described for making NaHCO_3 and a salt mixture containing NH_4Cl and KCl from natural mixtures of NaCl and KCl. For example, 0.5 l. of a solution containing KCl 1.27, NaCl 3.58, and NH_4Cl (from recycled mother liquor) 1.85 moles/l. was ammoniated with 1.2 moles NH_3 . The solution was then saturated at 40° with CO_2 (1.2 moles) causing precipitation of NaHCO_3 (pH 7.5). The mixture was vacuum filtered at 30° and the filter cake was washed with methanol, yielding NaHCO_3 free of impurities. The pH of the filtrate (8.4) was adjusted to 9.0 with NH_3 . Then the solution was mixed with 191 g of a KCl-NaCl mixture (for example, rock salt) containing 70% KCl, cooled to 10° , and filtered. The filter cake was washed with methanol, yielding a mixture of KCl and NH_4Cl suitable for fertilizer use, containing little or no NaCl or NaHCO_3 . The filtrate was recycled to NaHCO_3 precipitation step.

(*ibid*)

Cement and Sulphuric Acid from By-Product Gypsum

Comprehensive operational data has been released by VEB Konstruktions-und Ingenieurburo for utilization of by-product phospho-gypsum in the manufacture of cement and sulphuric acid—the process developed by VEB Chemiwerk Coswig in conjunction with Chemic—Ingenieurbau Leipzig of East Germany. In this process calcium sulphate is reacted with carbon by the Muller-Kuhne technique to yield sulphur dioxide as a gaseous product. The reactions take place in a rotary kiln at optimum temperatures of 900°C and 1200°C cement clinker is formed during the reaction by addition of clay, sand and iron oxide.

The raw materials and utilities requirements per tonne of monohydrate for plants

based on phospho-gypsum are given in the Table 1.

With the exception of the quantity of calcium sulphate-bearing material, which varies according to content of CaSO_4 , raw material requirements are essentially similar. Utilities, however, vary quite widely—phospho-gypsum requiring the most fuel oil, but natural gypsum requiring the most electric power and water.

Despite the very low raw material costs possible, when using phosphoric acid-gypsum as a raw material, the overall economics of the process are a different matter. The investment cost is of the order of seven times as great as for a sulphur-burning facility and particularly at a time when prices of elemental sulphur are generally falling, the importance of this factor must be accurately assessed for each specific location.

Single kilns can be produced with capacities of 150,200 and 350 tpd of monohydrate. Although 350 tpd is the largest single-stream capacity possible at the present time, larger capacities may be obtained from multiple units.

Product Quality and Yields: As would be expected, the process is capable of producing any grade of sulphuric acid or oleum, but product quality is a consideration which is more important to the by-product cement, and guaranteed strengths of cement produced by the process from different raw materials are shown for various setting times in Table 2. The strength of cement derived from phosphogypsum is quoted in the table as 325 kp/cm² after 28 days; this is a guaranteed figure and is considerably lower than the 376 kp/cm².

It is stated that, when using the process to regenerate sulphuric acid for the acidulation reaction in the manufacture of wet process phosphoric acid, more than 80% of the sulphuric acid requirement is regenerated. The remainder must be provided by conventional methods or by supplementing the cement/acid process feed with make-up quantities of natural gypsum, anhydrite or noncaptive phosphoric acid gypsum.

[*Sulphur* No. 86 (1970) 31]

New Urea Process from Montedison

Montedison SpA has developed a new urea process which is stated to offer increased heat recovery from recycle carbonate enhancing economics. A 700 tpd unit using this process has been operating and a 900 tpd unit is now under construc-

TABLE 1—CONSUMPTIONS PER TONNE MONOHYDRATE

Item	Phospho-Gypsum	Anhydrite	Natural Gypsum
Phospho-gypsum (94.5% CaSO_4), tonne	1.84		
calcined	1.71		
Anhydrite (95% CaSO_4), tonne	—	1.63	
Natural gypsum (75% CaSO_4), tonne	—	—	2.18
clay (25% Al_2O_3 , 51% SiO_2), tonne	0.27	0.27	0.27
sand (94% SiO_2), tonne	0.08	0.08	0.08
coke, tonne	0.13	0.13	0.13
iron oxide (pyrites cinders), tonne	0.01	0.01	0.01
natural gypsum (setting regulator) tonne	0.03	0.03	0.03
Electric power, kWh	200	200	215
Water (15°C), m ³	50	18	55
Fuel oil (10,000 kcal/kg), tonne	0.34	0.23	0.28
Credit: Cement production, tonne	0.95	0.95	0.95

TABLE 2—PRODUCT CEMENT STRENGTH FOR VARIOUS FEEDSTOCKS

	Phospho-gypsum	Anhydrite	Natural gypsum
Strength after			
3 days, kp/cm ²	100	200	150
7 " "	200	300	225
28 " "	325	400	350

[*Sulphur*, No. 86, January/February (1970), 31]

tion at the same site in Netherlands. The process is characterized by a high mole ratio of 3.4 parts ammonia to one part carbondioxide and a low $\text{H}_2\text{O}/\text{CO}_2$ mole ratio of 0.65:1. The water content of the recycle carbamate is lower than 20 per cent while the reactor efficiency is given as 60 per cent.

Process Details: Both pre-heated liquid ammonia and carbon dioxide are compressed up to the synthesis pressure of 200 atm and passed into the reactor operating at 200°C. The reactor effluent is transferred to the first decomposer/stripper unit operating at 80 atm and 190°C, where most of the carbamate is decomposed into ammonia and carbon dioxide. This first stripping process takes place at relatively high pressure but the pressure is still low enough to allow the decomposition of carbamate in equilibrium with the carbon dioxide and

ammonia, and there is no need to shift this equilibrium by addition of one of the reactant gases.

The vapours from the first decomposer/stripper enter the carbamate condenser where they are partially condensed to yield ammonia and an aqueous ammonium carbamate solution at a temperature of around 140°C. In this way, the gases from the first stripper, instead of being compressed, are condensed at the synthesis pressure under conditions suitable for steam production.

The gases not condensed in this first stage are separated in the second condenser which operates at the same pressure as the first, but at the greatly reduced temperature of 25°C. The inerts discharged from the second condenser are washed to recover any ammonia still remaining and then vented.

The carbamate solution brought down during the condensation stages is pumped back to the reactor. In order to cope with the extremely corrosive carbamate solution, piston pumps have been perfected to such an extent as to allow continuous and safe operation, and problems which involved seals, lubricants and construction materials have now been solved.

The urea solution, which is separated from the reactor effluent in the first stripper, passes through the second stripper at 12 atm. Effluent gases are sent to the third condenser where unreacted carbamate is separated in an aqueous solution and recycled to the first condenser.

Urea solution passes to the third stripper stage operating at 3.5 atm. From this unit 75 per cent urea solution is obtained and the gases separated are then recycled to the third condenser. The 75 per cent urea solution is concentrated in two stages under vacuum at 0.3 and 0.03 atm. respectively. Gaseous effluent from the first vacuum concentrator is vacuum condensed, and from the solution thus obtained ammonia is recovered in a rectification column. The gases flowing from the top of this column are condensed and recycled, while from the second vacuum concentration stage the 99.7 per cent urea melt is sprayed into the prilling tower.

An unusual feature of the process is that part of the carbon dioxides from the compressor is taken off at an intermediate stage at 80 atm. and directed to the first carbamate condenser. There is more heat recovery from carbamate recycle. A modest but not negligible reduction in power consumption is obtained due to the carbon dioxide feed being at the same pressure as the first recycle. All recycle ammonia in the condensers may be possible to recover thus avoiding the need to recycle liquid ammonia separately. Besides recovering condensation heat, the need to ammonia rectification, condensation and recycle apparatus in this section is eliminated.

The fundamental process, allowing for no steam export, consumes 900 kg of steam at 20 atm and 140 kWh of power.

Depending on the customer's power requirements, the process can be modified to give a significant export of low pressure steam, or the power necessary to drive the main machinery. When 1,100 kg of steam at 40 atm is imported, 250 kg of low pressure steam is available for export and the power consumption remains at 140 kWh. If, however, all the main machines are

driven by steam turbines, the consumption of high pressure steam is given as 1,250 kg, but the power consumption is reduced significantly to 10 kWh.

Economical urea production cannot be achieved unless an efficient method is employed to recover the unreacted ammonia and carbon dioxide. Total recycle processes differ little in principle, but their efficiencies and use of utilities vary considerably. The costs of cooling water and steam are important factors in the production cost of urea, and any means of recovering the heat of condensation of ammonium carbamate will reduce the consumption of these utilities. In this new Montedison process considerable attention is paid to heat recovery from the recycle carbamate, hence reducing the utility consumption and making the process more economical. In this respect the Montedison process compares favourably with other currently available urea processes.

[*Nitrogen* No. 63 Jan/Feb. (1970), 32]

New Phosphoric Acid Processes

A symposium on new phosphoric acid processes was held in London on Dec. 11 1969 arranged by the Fertilizer Society, wherein the following four processes were described: (1) The Albatros Phosphoric Acid Process by A. C. Van Es and J. Th. Boontje (VKF Mekog-Albators NV), (2) Dorr-Oliver HYS Phosphoric Acid process by W. C. Weber, E. J. Roberts, I. S. Mangat and E. Uusitalo (Dorr-Oliver Co. Ltd.), (3) Single-Stage Process for the production of 50 per cent P_2O_5 Phosphoric Acid by S. M. Janikowski and N. Robinson (Fisons Ltd.), and (4) The Kellogg-Lopker Phosphoric Acid Process by L. E. Bostwick and W. Turner.

Dorr-Oliver HYS Process: The new developed improvement on the wet process phosphoric acid has been given the name Dorr-Oliver HYS (High Yield and High Strength) phosphoric acid process. The process is now being employed in the commercial installation at Rikkihappo Oy's Siilinjärvi plant, Finland. The basic HYS process operated according to a system which is devised to simultaneously digest the rock, produce a strong acid and make a well-filtering and easily washed hemihydrate. This basic process, however, may be varied considerably, depending on the source of phosphate rock.

Phosphate rock is fed to the head end of a multi-tank cascading digestion system where it is reacted in pulp recirculated

from the vacuum cooler, which is normally operated in the range of 80 to 85°C. Number two filtrate from the hemihydrate filtration is also added to the first reaction vessel together with sludge from product acid-desulphation. Sulphuric acid of 93 to 98 per cent concentration is added to the downstream reactors.

The insoluble P_2O_5 content of the hemihydrate crystals is normally 1.6 to 2.0 per cent when producing 43 to 47 per cent acid. This is mainly P_2O_5 contained in the lattice; citrate-insoluble P_2O_5 is relatively low.

Pilot plant study has been done on Russian Kola apatite prior to the construction of the Rikkihappo Oy plant and also more recently on Florida and Morocco rocks. Kola proved to be the most difficult because of the slow rate of recrystallization of the hemihydrate, Dorr-Oliver reports, but with Florida and Morocco rocks the filtration rates for the recrystallized gypsum were fantastically high. Percentage moisture in the hemihydrate cake was in the range of 22 to 28 per cent with Florida the better, and 14 to 22 per cent for the gypsum filter cake with Morocco generally the better. With Kola rock, it is possible to get very high filtration rates on the hemihydrate but considerably slower gypsum rates due to the gypsum crystal shape. It should be noted that the total active filtration area required for the HYS process is somewhat more than for the conventional dihydrate process, depending on the strength of acid produced and the rock used. However, the larger filter required offset by the elimination of considerable evaporation equipment and operating cost.

The amount of insoluble P_2O_5 which remains in the recrystallized gypsum on a dry gypsum basis is about 0.18 to 0.22 per cent for both Florida and Morocco rocks. Of this, less than 0.05 per cent is nitrate-insoluble, the factor for converting P_2O_5 in gypsum to loss as per cent of P_2O_5 fed is about 4.5 to 4.6 for both Florida and Morocco rocks, and the insoluble losses are just about 1 per cent of the P_2O_5 fed. There is stated to be no problem in producing 45 per cent P_2O_5 with any of these rocks.

By eliminating the steam requirement for evaporation, in an integrated plant the use of the by-product steam from the sulphuric acid plant for power production can be economically attractive. Indeed, it is indicated that it is possible to make the phosphoric acid plant independent of outside power.

Albatros Process: The process is similar to processes developed by Nissan, NKK, and Mitsubishi of Japan and with the U.S. Singmaster and Breyer process. The processes are, in fact, based on the series of patents of the Kunstdunger Patent Verwer-tungs AG 1928-1933 (M. Larsen U.S. patent 1,836,672 December 1931).

The purpose of the first of the two reac-tors is to accomplish an almost quantita-tive dissolution of the phosphate rock in phosphoric acid prior to the precipitation of hemihydrate. Rock is intimately mixed with recycled phosphoric acid/hemihydrate slurry, sufficient for complete dissolution. The reactor is fitted with a central tube co-axial with the agitator shaft and adjust-able in height so that it skims off the surface of the liquid and it is used for rapid dis-persion of the phosphate rock in the slurry vortex. This arrangement effectively destroys foam.

The slurry emanating from the phos-phate dissolution reactor and containing almost 4 per cent dissolved lime in excess of the corresponding sulphate content goes to the hemihydrate crystallizer, where coarse crystalline hemihydrate is formed by the careful addition of concentrated sulphuric acid.

Special factors to be taken into account are: sufficient high solid content in the slurry (up to 30 per cent by weight), presenting crystal surface area; efficient but gentle mixing to minimize local super-saturation without destroying the growing crystals. Temperature must be held above 100°C.

VKF Albatros-Mekog reports very good results and were accomplished in a special reactor design—the Rotating Disc Reactor. This reactor ensures gentle but thorough stirring and the distribution of sulphuric acid feed over several injection points.

Average residence time in the hemi-hydrate reactor is up to 15 min. for ground Taiba phosphate rock; residence time in the phosphate dissolution reactor is 6 min. and for unground rock 15 min. In both cases dissolution is almost 100 per cent, but with unground rock the reaction is less violent and foaming is better controlled.

The second step is the recrystallization of the impure hemihydrate to dihydrate, setting free the entrapped P_2O_5 in order to obtain high recovery of P_2O_5 . Research has shown the benefit of recrystallizing in a solution with a high sulphuric acid content, up to 20 per cent. This high sulphate level has two advantages, viz. (1) Extremely low

P_2O_5 level in dihydrate gypsum (lower than 0.1 per cent) and (2) increased rate of re-crystallization of the hemihydrate crystals to the dihydrate (gypsum) form.

The hemihydrate is washed with filtered recrystallization solution from the dihydrate filter. The filtrate from the hemihydrate filter containing up to 10 per cent SO_4 is recycled to the hemihydrate reactor. The dihydrate is filtered and washed twice on a belt-type filter. The resulting pure gypsum is a raw material well-suited for several purposes.

The hemihydrate directly produces phos-phoric acid of a strength of up to 5.2 per cent P_2O_5 without the need of a concentra-tion plant. Savings are calculated at about £ 3-4 per tonne of P_2O_5 in acid. There is a better than 99.5 per cent recovery of P_2O_5 . Also, there is better utilization of sulphuric acid. The resulting better-formed crystals give higher filtering rates and because of the better control of the chemical reactions in question no excessive reactor volumes have to be installed in order to reach the desired recovery and crystal size. For cool-ing and for fluorine recovery a flash cooler will have to be installed in the hemi-hydrate section.

Kellogg-Lopker Process: Although it was announced over a year ago, details of the Kellogg-Lopker phosphoric acid process have been lacking. At the Fertilizer Society meeting, L. E. Bostwick and W. Turner of M. W. Kellogg Co. in New York, U.S.A., and Kellogg International Corp. in London respectively, disclosed that the reaction system for this process consists of two vessels interconnected to provide a recir-culating flow path with the two vessels

being offset vertically. The slurry is pumped into the lower vessel—known as the dis-solver—and passes through this vessel to the upper vessel—known as the evaporator. The slurry returns by gravity from the evaporator to the dissolver. The evaporator is maintained in a vacuum, while the dis-solver is at atmospheric pressure. Flow of slurry in the system is downward to the dissolver and through the pump to the evaporator, where it enters approximately tangentially and imparts a rapid swirling motion to the evaporator contents. The slurry then flows downward in the evapo-rator through to the dissolver, which it also enters approximately tangentially. The downward flow in both vessels eliminates the possibility of settling of solids.

Phosphate rock and recycled phosphoric acid swirl from the filter system and feed into the dissolver and swirling action is designed to effect mixing in the recirculating slurry. In the evaporator sulphuric acid is distributed and this mixes with the swirling slurry.

Compared with the conventional digester the back mixing is minimal and the high recirculation rates reduce temperature differentials in the system.

The attack and crystallization operations can be more carefully controlled with a saving in grinding and filtrations. The eco-nomics of the operation were indicated by the authors for 68 per cent TPL Florida rock and 77 per cent sulphuric acid feed in the plant of 1,000 tons p.d. capacity of P_2O_5 . Acid concentration in excess of 40 per cent P_2O_5 can be obtained by opera-tion of the hemihydrate route by alterations in the parameters.

KELLOGG-LOPKER PROCESS: ECONOMICS OF OPERATION

	Kellogg-Lopker	Conventional	Reduction with Kellogg-Lopker
Capital investment rates	0.8	1.00	20%
Operating manpower per shift	3	4	25%
Maintenance, % of capital	5%	6%	16%
Utilities per ton of P_2O_5			
Power kW/hr	53	145	63%
Process Water—Gal	1,000	1,000	0%
Cooling Water—Gal	12,000	12,000	0%
Steam—lb	1,800	1,800	0%

[Fertilizer International, No. 9, March (1970), 9]

Phosphoric Acid Production and Operation Problems

A group discussion on phosphoric acid production and the operation of the phosphoric acid plants involving innumerable problems was held at FACT, Alwaye (Kerala) on Sept. 18, 1969. Seven technical papers were read by delegates from G.S.F.C., Coromandel, FACT, EID-Parry, DMCC and Dorr-Oliver India Ltd. Many eminent engineers from phosphoric acid plants participated in the discussion.

In the phosphoric acid production, the main raw material—rock phosphate—in addition to having tricalcium phosphate contains varying quantities of iron, aluminium, silica, fluoride, chloride, carbonate and organic matters and each of these contributes to the difficulties experienced during the phosphoric acid production. Because of problems, continuity of production is hampered. Even in USA there is not a single wet process phosphoric acid plant running continuously for a month with at least 90 per cent of its rated capacity. The only record of continuous running for $4\frac{1}{2}$ months has been in electrothermal phosphoric acid plants. Improvement in the yield of phosphoric acid and possible production of high concentrated acid directly without resorting to evaporation are important aspects of production. Plants should run at optimum rate with optimum efficiency. Instrumentation is the most difficult area in the fertilizer plants. For smooth production, proper maintenance of machinery and instruments is necessary. Stress on the indigenous manufacture of essential equipment and spare parts required in the phosphoric acid plants should be given and phosphoric acid producers at a concerted effort should pool their resources and get some Indian parties to manufacture the equipment they require.

The following points were discussed while reading the papers: (1) Raw Materials, (2) Reaction and Filtration, (3) Concentration, (4) Product Acid and By-product, and (5) On-Stream Efficiency.

The raw material—phosphate rocks—is from different deposits. It varies widely in composition and P_2O_5 content and these variations and impurities contained affect the phosphoric production. The CaO/P_2O_5 ratio is important since it determines the acid requirement with each rock, the process controls have to be changed to get efficient digestion and recovery of P_2O_5 . The indigenous Rajasthan rock contains more iron and alumina and lower P_2O_5 than what is normally contained in the Jordanian

rock. Also, the indigenous rock is very hard and difficulties have to be faced to grind them. During the reaction stage P_2O_5 is held back. The authorities should arrange that the only imported rock of particular quality is sent to the factory so that it has to tackle the same type of problems every-time. A specification for the acceptable rock grade should be made. Udaipur rock needs beneficiation and this could be blended with superior rock for use.

The general desirable composition of usable rock phosphate should be as follows: P_2O_5 32 per cent, Chloride as sodium chloride 0.15, CO_2 4.5, SiO_2 2.5-3, Fluorine 2.5-3, R_2O_5 3.0 and organic matter 1—2 per cent.

The location of equipment and pipe lines, etc. should be so arranged as to enable attending to the scaling problems and checking the tendency of the materials handled. Care has to be taken to efficient dust collection system and there should be efficient dust filters to make the atmosphere free from pollution.

Moisture content in the rock phosphate should be less than 2 per cent otherwise drying will be expensive. There is considerable foaming in the attack tanks due to the presence of organic matter. Oleic acid is used as an anti-foaming agent. There are losses in grinding and handling.

Ms rubber-lined shafts for agitators are used which are available indigenously. Indigenous filter cloth is also used which works satisfactorily. The process of reaction and filtration should be carried out in such a manner that downtime is minimized. Corrosion problem is also not severe. The strength of the sulphuric acid has to be controlled.

Concentration: The problem of concentration is very acute in some plants; problems may be in the circulation pump and in the cleaning of calandria to reduce the duration of downtime.

Product Acid and By-Product: P_2O_5 product of more than 75 per cent is unnecessary. The plant is operated for 250 days. Average soluble— P_2O_5 in the gypsum varies between 0.3 to 0.5 per cent.

The recovery of P_2O_5 for the rock is 93-94 per cent. The recovery is very important not only from the point of yield but also quality of the gypsum. Phosphogypsum can be used to manufacture sulphuric acid plant. Phosphoric acid plant can be run from 250-320 days. For proper maintenance, spares of right materials of

construction are necessary; it may be possible to use indigenous material.

(FAI Proceedings, 1969)

Management of Science

A national seminar on management of scientific research laboratories was held during Oct. 10-12, 1970 under the joint auspices of the Committee on Science and Technology (COST) and the Administrative Staff College of India (ASCI). The discussion covered the problems relating to the following topics: (1) decision-making at laboratory—organization structure and leadership; (2) research planning and programming and criteria for the choice of projects; (3) the infra-structure—physical and informational; (4) management controls—financial and budgetary; (5) personnel—policies and practices; (6) evaluation of research and development; (7) relationship of the laboratory with other R and D organizations and professional scientific bodies; (8) relationship of the laboratory with the actual and potential users; and (9) relationship of headquarters organization with the Governmental decision-making bodies and the impact on the laboratory.

Personnel Problem: The problems of scientific and technical personnel in R&D organizations engaged considerable attention. The productive intellectual activities of such personnel need a fair degree of flexibility and freedom to promote motivation and leadership for creating new ideas. The orthodox style in recruitment policy is not suitable to obtain the right type of R and D personnel; some amount of 'talent hunt' is necessary. Recruitment at fairly senior level through negotiations was found to be one of the effective methods.

Stress was given on a suitable promotion policy for the R & D personnel, who are at present able to go up the ladder only through the process of fresh selection in open competition. It was felt that promotion through assessment of work every 3 to 5 years would be desirable in all scientific and research organizations for encouragement to continuous good work and to eliminate stagnation. Such promotion on evaluation would virtually mean upgrading of post without having to expand the staff structure. It is generally noticed that the pyramid is very flat at the base. The descriptive annual confidential report, as used in civil service, was found not suitable for rating scientists and research workers. Two assessment forms were presented.

Multiplicity of pay scales as obtainable at present was not favoured and streamlining was recommended. The distinction between scientific and technical grades should be abolished. Technicians are also to get encouragement and fair deal. To prevent obsolescence in scientific thought and techniques, efforts for development of personnel and career planning can be made internally as well through sabbatical leave system and participation in national and international conferences. Mobility between research laboratories, universities and industry would also help.

The COST-ASCI seminar did not propose any revolutionary change but had clearly brought but the obvious lacunae needing rectification. Many of the points have been considered and reiterated many times previously but remained as ritualistic exercises. Some of the following personnel policy questions are neither revolutionary nor abnormal: equal pay structures and status for scientific and technical employees with administrative personnel; mobility; flexibility in working conditions; adequate promotion and reward systems, objective evaluation of performance; arrangements for keeping them up-to-date through retraining, career development programmes, sabbatical leave and other processes; participation of scientists in policy-making; freedom of communication, etc. It is hoped that the recommendations of the Hyderabad seminar will be implemented soon.

[*Technical Manpower*, CSIR, 12 (10) (1970), 1]

Conference of Scientists

In inaugurating a 3-day conference of scientists, technologists and educationists, organized by the Committee of Science and Technology (COST) of the Government of India, on November 28, Smt. Indira Gandhi, Prime Minister, expressed her hope that this conference would give specific directives to scientific and techno-

logical activities of the country in relation to the vital needs. Dr. B. D. Nagchaudhuri, Chairman of COST, said that larger funds were now being spent on research and development (R & D) and therefore the question of effectiveness of R & D became pertinent. Though science policy includes technology, Dr. V. Ranganathan, Secretary of the COST, drew special attention to the importance of technology in the present context of one national economy. About 140 delegates, who attended the conference, divided themselves into 4 groups dealing with (i) science policy, (ii) climate and management of science, (iii) reorganization of R and D structure, industrial development and transfer of technology and (iv) higher education and manpower.

Though the problems of scientific and technical personnel figured as a specific subject for discussion in a particular group, the topic cut across the group barrier and figured in other group discussions as well. The conference observed that higher education in science and technology needed improvement with addition of certain new subjects particularly of inter-disciplinary nature. The university sector needed greater support, specially on the research side. At present, there is no specific head for research in the universities. The university research is carried out in bits and pieces through *ad hoc* grants and other forms of support from organizations, like CSIR, UGC, AEC, etc. The conference observed that for post-graduate departments, the number of professors, readers, etc. should not be tied up with the norm of teacher-student ratio. The number of teachers should depend on research potential and programme of the department.

The conference desired that there should be more linkage between the universities, R and D organizations and industry for making all the three sectors more effective and viable. On the point of unemployment

among scientists and engineers, the conference noted that there were a large number of unfilled vacancies in the country and recommended that efforts be made to make an optimum utilization of the employment opportunities that already existed. The conference observed that there were many areas of much-needed scientific and technical activities, such as techno-economic surveys and feasibility studies, quality control in production, writing of technical project reports, assessment of natural resources, etc. which could open up a considerable degree of low cost employment of great national utility. The effect of foreign collaboration on national employment situation needed to be studied in depth. Other employment avenues were also discussed.

To promote healthy mobility of the scientists, the conference observed that the scientists should be enabled to change their jobs and carry their service benefits from one organization to another. Uniformity or comparability of salary structures would also help mobility.

In recruitment of scientific and technical personnel, the method of 'talent hunt' was considered better than that of impersonal advertisement, particularly at senior levels. Promotion of scientists, who are usually specialists in their respective fields, should depend on their performance, and not on the availability of suitable vacancy.

Enunciation of national objectives and identification priorities are necessary. Science Plan should follow Science Policy. A national apex body may be entrusted with the task of evolving Science Plan and fixing priorities—it may be the COST or restructured COST, or one with a new name, like National Committee on Science and Technology (NCST), which should have firm links with the Planning Commission.

[*Technical Manpower* (CSIR), 12 (12) (1970), 1]

Prof. C. V. Raman, Nobel Laureate

(Nov. 7, 1888—Nov. 22, 1970)

Chandrasekhara Venkata Raman passed away on November 22, 1970 at the age of 82. An active physicist till the end, he exhibited scientific brilliance at the age of 16 when his first paper on diffraction band of light was published in the *Philosophical Journal* of London. He received Nobel Prize in Physics for 1930.

Raman took his B.A. and M.A. degrees from Madras University standing first in both and entered the Indian Finance Department in 1907 as an Asst. Accountant-General. During his posting at Calcutta, he spent long hours on experimental research in his spare time at the Indian Association for the Cultivation of Science, founded by Dr. Mahendra Lal Sarkar.

Raman's interest was in many scientific fields, besides optics. His researches spread over acoustics of musical instruments, crystallography, physiology of colour vision and perception of sound. 'Raman effect' (1928) deals with the scattering and modification of light when it passes through a transparent substance. Using a monochromatic light, a small fraction of it gets scattered by the molecules of the substance. The scattered light is no longer monochromatic, and new spectral lines appeared by the side of the original one. This means that the original wave length has suffered modification after interaction with the molecules of the scattering medium. Since each kind of wave length represents a particular energy content of the light, the modification so obtained is an indication of sharing of energy between the original light and the molecules. The new lines are known as Raman lines, to distinguish them from the original spectral line, and the amount of energy in them can be measured spectroscopically. The modifications in them depend on the nature of light used as well as the molecules of the substance with which it interacts.

Raman's experiments and interpretations have opened a new approach for understanding the molecular configurations and binding energies of atoms in a molecule and have therefore a direct application, so much so that scientists all over the world started work on it.

Raman joined Calcutta University as Palit Professor of Physics in 1917 at the invitation of Sir Asutosh Mukherjee and remained there till 1933. He was knighted in 1929. He joined the Indian Institute of Science, Bangalore in 1934 where he started the fortnightly journal, *Current Science*. He helped the formation of the Indian Science Congress Association in 1921 and was twice President of the Physics Section. He founded the Indian Academy of Science (1934). He was awarded *Bharat Ratna* in 1954. He became FRS in 1924, received Hughes medal of the Royal Society and was awarded Franklin medal of Franklin Institute, USA, of which he became a Fellow. He received Matteucci medal, Rome, and became the President of the Indian Science Congress in 1928. He also became a Fellow of the Royal Irish Academy and obtained the Lenin Peace Prize (1957). He was a Foreign Member of Soviet Academy of Science (1957) and Foreign Associate, Paris Academy of Science (1949). He became Pontifical Academician (1961) and Hon. Fellows of Hungarian, Czechoslovak and Rumanian Academies of Science and also of the Chinese Physical Society. He was National Professor (Physics) of India since 1949. After retirement he founded Raman Research Institute of Science in 1943 at Bangalore, where he continued his researches till his end. Raman avoided committees and commissions and did not agree with space programmes research. He was critical of giant laboratories.

News in Brief

Phosphoric Acid Through Ammonium Sulphate

The two new non-sulphur processes for production of phosphoric acid, developed by B. D. Bohna & Co. USA, use ammonium sulphate as the principal reactant and are claimed to produce directly superphosphoric acid. In the first process—called RABS process—the raw materials are rock phosphate and ammonium sulphate, while in the second R2 process—single or triple superphosphate and sulphuric acid or ammonium sulphate form the raw materials.

In the RABS process, direct reaction between phosphate rock and ammonium sulphate takes place by double decomposition of calcium sulphate and ammonium phosphate, the latter decomposing to ammonia and phosphoric acid. Calcium sulphate is processed to ammonium sulphate for recycle, which requires a small amount of make-up ammonia. This process can compete with the conventional wet process routes based on sulphur costing 20-25 per short ton; capital, maintenance and labour costs are approximately the same.

The R-2 process involves interaction of single or triple super phosphate and sulphuric acid to produce phosphoric acid and gypsum. It also works with ammonium sulphate in place of sulphuric acid, when ammonium phosphate decomposes to ammonia and phosphoric acid.

The superphosphoric acid (72 per cent P_2O_5) produced by either processes contains less impurities and is less viscous which simplified storage and transportation. It can be ammoniated to obtain the new ammonium polyphosphates (15-61-0) or the conventional polyphosphates such as 12-62-0 and 21-54-0. Fertilizer solutions could also be produced.

[*Fertilizer News*, 15 (8) (1970), 34]

Iran to Cut Price of Ammonia

Iran has at last agreed to cut price of ammonia to be supplied by it for use in fertilizer plants to be set up in India. The reduction is said to be about R. 5.50/tonne. The actual price of ammonia after latest

reduction is believed to be about Rs. 255/te. The reduction was secured by FCI Ltd. in the course of negotiations with the National Petroleum Co. of Iran. The ammonia to be produced will be set up by Shahpur Chemicals, a subsidiary of the Iranian Company.

[*FAI Inf. Serv.* 11 (17) (1970) 7]

Fertilizer in Cooperative Sector

The Indian Farmers Fertilizer Cooperative, which is setting up a giant Rs. 90-crore fertilizer complex, formally took over 236 acres of land at Kalol for its 910 tonne/day ammonia and a 1200 te/day urea plants. Another part of the complex, including a 400,000 NPK (4:2:1) plant, will come up at Kandla. The ammonia plant at Kalol will be based on about 7.5 lakh cu.m. of natural gas to be supplied by ONGC. Ammonia will be transported from Kalol while phosphoric acid and potash will be imported.

IFFCO's shares will be held by co-operatives in 10 states. Working in close cooperation of this complex will be American fertilizer producing cooperatives, who have formed a no-profit foundation to provide technical and managerial assistance. The foreign exchange needs of the complex would amount to about Rs. 25 crores and a consortium of Indian financing institutions would loan about Rs. 50 crores. About future plan the organization would consider the setting up of a Rs. 12 crores phosphoric acid plant.

[*FAI Inf. Serv.* 11 (17) (1970), 8]

Phosphate Concentrate from Rock Phosphate

On behalf of the Hindustan Zinc Ltd., tonnage quantities of phosphate concentrate were produced from phosphate rock from Udaipur for the production of superphosphate at the National Metallurgical Laboratory, Jamshedpur.

Studies carried out at NML on the phosphate rock from Marsana block (Mussoorie, U.P.) showed that the rock

can be upgraded to produce concentrates suitable for superphosphate manufacture. Pilot plant trials on the production of silico-chrome by single stage electric smelting process were successfully completed for the Ferro-Alloy Corpr. Ltd., Garividi. The process consists in simultaneous reduction of chromite and quartzite with carbonaceous reducing agents, like coke, ltc coke, charcoal, etc., to yield a product containing silica (40-45), chromium (35-40) and carbon (0.05 per cent). The power consumption per tonne of the alloy produced is 7800 kWh.

[*CSIR News*, 20 (19) (1970), 14]

A New Process for Potassium

Salt Lake City, Metallurgical Centre of the U.S. Bureau of Mines has developed a process based on ion-exchange system for recovering potassium. It is applicable to sea water or end bitterns and involves selective precipitation of potash and subsequent recovery of the precipitant.

[*Salt Res. & Indus.*, 7 (1) (1970), 30]

Shortage in Potash Consumption

The Director of Potash Fertilizers Ltd. stated that although the use of potassic fertilizers in India has increased from 10,000 to 2,00,000 tonnes, the consumption of the three main nutrients N:P:K during 1967-68 was 1:0.39:0.18 against 1:1:1 in the agriculturally well-developed countries. He stressed that use of more proportion of nitrogenous fertilizers may lead to reduction in yields if potassium is not added in the required proportion.

(*ibid*)

Salt-Based Fertilizer Plant

A Rs. 12 crore salt-based fertilizer plant, manufacturing ammonium chloride and other by-products is to be located near Bombay. It will also manufacture 66,000 tonnes of soda ash and serve as a nucleus for the development of industries for fertilizers and agricultural chemicals.

(*ibid*, 32)

Plant Breeding at the Indian Agricultural Research Institute

The Director of IARI told the seminar on Application of Nuclear Tools in Agricultural Research, held recently at New Delhi, that if the technique of crossing between the cells of different crop plants like wheat and maize and wheat and rice, being attempted in his Institute, become successful it would open up a new era in plant breeding. Among the principal achievements in recent years were: Sharbati Sonora variety of wheat, Jagannath variety of rice and Aruna variety of castor. The Aruna castor, which took only about 110 days to mature as compared to 250 days of the cultivated varieties, was becoming popular in Telengana region. Several mutants including one of barley had been developed with a better quality.

The use of radio-isotopes had become valuable in studying the rooting pattern of crop plants, which could help in developing plants with a deeper root system for the dry farming regions.

[*FAI Inf. Serv.*, 9 (21) (1970), 8]

7 Per Cent Growth in World Fertilizer Demand

An increase in the world fertilizer consumption of 7 per cent a year until 1975 slackening to 5.5 per cent in the following years has been forecast by the Tennessee Valley Authority in a study for the U.S. Agency for International Development. If these growth rates are borne out, world consumption of nitrogen, phosphorus and potassium will reach 89 m. metric tons in 1975 and 115 m. tons in 1980 compared with the present consumption of 64-65 m. tons. Present output capacity is 82.5 m. tons.

On the above forecasts, British Sulphur Corporation's Journal, Fertilizer International, says that the Authority's estimates of the developed region's consumption are lower than those made in a similar study in 1968 due to a reassessment of the fertilizer use factors and to lower population growths. The developed areas of the world are now expected to use 66 m. tons in 1975 and 81 m. tons in 1980, while developing regions should absorb 24 and 34 m. tons respectively.

The expansion in nitrogen capacity is still outpacing consumption, but present capacity plants indicate a supply-demand balance in nitrogen by 1973, with some further additions supportable by consumption in 1979. The announced phos-

phate capacity exceeds the estimated requirements during 1974 and 1975 and the potash margin of production capacity to consumption appears high for all the 1974-75 survey period.

(*ibid*, 7)

Ammonia Glut

Western Europe is heading for a situation of ammonia over-capacity, which will probably depress prices for the next 3-4 years. The reasons are two-fold: (1) too many plants in the 1000 metric ton/day range are coming; (2) the fertilizer market is over-supplied. This makes producers to sell rather than use captively their ammonia output.

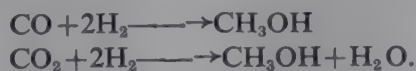
Faced with slumping ammonia prices and high interest rates on new-plant investment, BASF of W. Germany recently scrapped plans to build a plant in Antwerp. Instead, it will purchase 200,000 metric tonnes/yr. of ammonia from Nederlandse Stikstof—a subsidiary of Montedison—and supply it to Bayer and Degussa.

Belgium's Ammoniaque Synthetique et Derives (ASED), which owns a 100,000 metric ton/yr. plant is contemplating to shut down older plants. The small ammonia producers of France are ready to band together to build several large-scale installations. In Netherlands, most of the new plants (using natural gas) operate side by side with the older units, which has the effect of boosting overall ammonia capacity.

[*Chem. Engng.*, 77 (18) (1970), 32F]

Low Pressure Methanol Process

In the Lurgi's low pressure process, carbon monoxide, carbon dioxide and hydrogen are converted at 200-300°C, 400-700 psig in the presence of a copper-bearing catalyst, according to



The feed gas is compressed to synthesis pressure in a turbo compressor before it is mixed with the circulating gas. After passing through heat exchanger, the mixture enters reactor which enables a very gentle treatment of the catalyst. The methanol bearing gas leaving the reactor is cooled in a heat exchanger with circulating gas and in a cooler with air or water. The heat set free during methanol formation is utilized for generation of high pressure steam.

The condensed crude methanol enters a

separator for the separation of the gas which is returned to the reactor by turbo compressor for use as circulating gas. The flashed crude methanol from the separator is processed to pure methanol in the subsequent distillation plant. The relatively low synthesis pressure permits the use of steam turbine driven turbo-compressors in plants with a daily capacity of 150 tons and above.

[*Chem. Age of India*, 21 (7) (1970), 686]

ONGC Plans for Gas Utilization and Use of New Equipment

The Oil & Natural Gas Commission has prepared an integrated plan extending over a period of 15 years for production and utilization of gas from Ankleshwar, Cambay and various small gas fields of S. Gujarat worked as a grid. The total production of gas from the South Gujarat fields is estimated to increase from 1290 lakh cubic metres/day in 1970-71 to 13.73 lakhs/day in 1972-73. According to available estimates, 7.5 lakh cubic metres/day of associated and non-associated gas would be available from Kalol-Sanand which is the quantity committed to the Indian Farmer's Fertilizer Cooperated, but the off-take will materialize only around 1972. Till then ONGC is exploring the possibility of supplying associated gas on a short-term basis to some of the industries near Ahmedabad.

ONGC will use sophisticated digital seismic equipment for exploration in the Calcutta-Bodra region of W. Bengal during the coming field season. Favourable oil structures are believed to be present in this region at great depths. Four digital seismic units have been ordered for the above region.

[*Lok Udyog*, 4 (5) (1970), 599 and 601]

Research on Dry Land Farming

The Indian Council of Agricultural Research has sponsored a Rs. 1.48 crores coordinated research scheme on dryland farming, which will operate at 24 centres in different agroclimatic and social conditions in different Indian states. The Canadian Government is providing the necessary aid. An All India workshop attended by eminent soil scientists, agronomists, agricultural engineers, meteorologists and plant physiologists of the country will be held soon to develop the detailed programme. The Department of Agriculture at the Centre is taking up pilot projects on dry farming in many

states for which about Rs. 20 crores have been set apart. The recent break-through in irrigated agriculture is leading to growing disparity in income between irrigated and unirrigated regions.

Power Deficit After 1973-74

Unless an installed capacity of 26 million kilowatt of electric power is created by 1973-74, India would be facing increasing power deficits in the remaining years of IV plan. The 6th annual electrical power survey committee headed by Sri K. A. Dave, Chairman of Central Electricity Authority, estimates that demand for power would reach 18.5 million kilowatt by 1973-74. This would need an installed capacity of 26 million kilowatts. The IV plan target is 23 million kw of installed capacity.

The forecasts of the survey is that the peak load, the firm capacity and the deficit of public utilities would be: 1970-71—11229 mw (peak load), 10624 mw (firm capacity) and 605 mw (deficit); 1971-72—12794 mw, 11399 mw, 1395 mw; 1972-73—1440 mw 12725 mw, 1682 mw; 1973-74—17022 mw, 15149 mw, 1873 mw. The survey report says that the committee's estimates of availability of generating capacity upto 1973-74 are based on power development schemes which have already been approved. If the loads forecast from the committee are to be met it will be necessary to sanction additional schemes for augmenting the generation and transmission facilities in advance as benefits from conventional thermal generation schemes accrue only after 4-5 years from the date of sanction which the gestation period for nuclear and hydroelectric projects is even longer. The survey allows for about 1.5 million lift irrigation pump sets and tubewells to be energized in the 4th plan period.

Agriculture Commission

Government of India has announced the composition of the national commission on agriculture set up recently under the chairmanship of the former Food Minister, Sri C. Subramaniam. Full-time members are: Dr. S. K. Mukherjee, Vice-Chancellor Kalyani University; Dr. H. R. Arakeri, Director of Agriculture, Mysore; Dr. P. Bhattacharyya, retired Animal Husbandry Commissioner.

Part time members are: Sri M. V. Krishnappa; Sri Randhir Singh; Dr. Z. A. Ahmed (all MPs); Dr. M. S. Swaminathan, Director, IARI; Dr. D. P. Singh, Vice-

Chancellor Agricultural University, Pantnagar; Sri T. A. Pai, Chairman, LIC; Sri B. S. Nag, formerly Adviser Planning Commission; Dr. A. M. Khusro, Institute of Economic Growth, New Delhi; Sri Hari Singh, Retired Inspector General of Forests; Sri N. K. Panikkar, National Institute of oceanography.

New Ammonium Sulphate Process

In the existing commercial process for the production of ammonium sulphate, the material is produced initially as an aqueous solution that must subsequently be concentrated to yield the solid crystalline product which is normally required. A new process described in a British patent, recently granted to Continental Oil Co. of Delaware U.S.A., in which the solid product is produced directly from the process reactions, thus eliminating the need for evaporation and crystallization equipment which, at the present time, form an integral part of ammonium sulphate manufacturing plant.

The technique, involves the use of gaseous feedstocks, sulphur dioxide, ammonia and oxygen, and the reactions take place in an alcohol solution of an organic amine with a basicity greater than that of ammonia. Sulphur dioxide, together with a stoichiometric quantity of water is first absorbed in the amine solution to produce an amine sulphite which is later oxidized to the amine sulphate by addition of oxygen or air to the solution. On addition of gaseous ammonia to the solution, ammonium sulphate is formed, with the regeneration of the amine which can be subsequently be recycled. Under the conditions of the reaction, the ammonium sulphate is insoluble and is thus obtained directly in crystalline form and only needs to be dried. A large number of amines can be used, the only specific requirement being that amine should have dissociation constant of at least 9.25. Reaction temperatures are relatively low, not exceeding the boiling point of the solvent. Gases containing only trace amounts of sulphur dioxide can be used, since the strongly basic amine absorbs sulphur dioxide very efficiently, and an additional advantage of using a strong base is that the ammoniation reaction is endothermic thus obviating the need for heat removal at this stage.

[*Brit. Patent*, 1, 165, 965; *Sulphur* No. 86, Jan/Feb, (1970) 30]

Ammonia Reduces Cost of Cattle Feed

Nitrogen additives for cattle fodder

should be considerably cheaper within the near future, following the discovery by researchers at Michigan University that ammonia can be used instead of urea in this capacity. Ammonia is approximately one-third the price of urea in the U.S., and unlike humans, ruminants are able to utilize simple nitrogen fixations to form amino-acids, the basis of protein.

The Michigan research team have developed an additive, Prosil, consisting of an ammonia solution and various trace elements, which can be mixed with silage fodder corn. Prosil could be marketed, initially in Michigan, at around 80 per s. ton.

[*Nitrogen*, No. 63 Jan/Feb. (1970), 34]

North Sea Oil

The discovery by British Petroleum of a major oilfield under British waters, a few months after the discovery by Phillips Petroleum of a similar field under Norwegian waters confirms the North Sea as one of the world's great areas of oil reserves. Europe has not suddenly become, in respect of oil, independent of the Middle East but a big source of supply in European territory shifts the balance considerably.

Almost as difficult to assess as the likely total of these North Sea reserves are the economics of exploiting them. In respect of both exploration and exploitation, conditions in the North Sea are peculiarly difficult and the difficulties will be reflected in prime costs much higher than in the Middle East. On the other hand, percentage payments to producing countries are much higher in the Middle East than in Britain, and the cost of transport from ME is at present phenomenal. If the latest stimulus generates a rapid advance in undersea technology North Sea oil will evidently be competitive.

[*The Statesman*, 26-10-70]

Purisol Process of Gas Purification

It is a physical adsorption process used chiefly for removal of carbon dioxide, hydrogen sulphide and acidic components from high pressure gases, natural gas, synthesis gases, etc. It is basically different from the chemical absorption processes, such as the well-known amine and hot carbonate processes. Physical absorption is preferable when the component to be removed has a high partial pressure.

The economics of the process depends mainly on the properties of the solvent; this process uses N-methyl-pyrrolidine

(NMP) as a solvent, which is particularly suitable for carbon dioxide and hydrogen sulphide absorption and permits operation at temperatures just above the ambient temperature, thus saving costly heat exchangers. The process heat can be removed by air or cooling water. The following are some of its applications. (i) removal of carbon dioxide from shifted gas produced by oxidation of heavy crude or residual oil to obtain high pressure hydrogen for hydrocracking or ammonia synthesis; (ii) carbon dioxide removal from compressed shifted gas produced by reforming natural gas or naphtha (iii) removal of carbon dioxide from natural gas and synthesis gas with high carbon dioxide and low C_2 content; (iv) bulk removal of hydrogen sulphide from natural gas with high hydrogen sulphide content; (v) removal of hydrogen sulphide from carbon dioxide—

bearing natural gas or synthesis gas with low H_2S/CO_2 ratio with the requirement to produce an off-gas with a high hydrogen sulphide concentration for economic processing in a Claus kiln.

[*Purisol for Gas Treating*, booklet issued by Lurgi Gesellschaft, Frankfurt.]

Lurgi Coal Gasification Plant

Vidharva Chemicals & Fertilizers Ltd., promoted by M/s. Karamchand Thapar & Bros., Calcutta, are going to have a Lurgi plant for gasifying non-caking coal (vol. matter 29, ash 17, moisture 10 and fixed carbon 44 per cent; cal. value 5,400 Kcal/kg.) at Kamptee (Nagpur) for manufacturing 500,000 tonnes/yr. of urea. The project has been approved by the Government of India and a letter of intent has been issued. Its feasibility

report was prepared by Engineers India Ltd., who proposed the capacity as 750 te/day of ammonia and 1,310 te of urea. The final proposed capacity, however, stands at 900 te of ammonia and 1,500 te/day of urea by total recycle process. Maharashtra State Industrial Development Corporation are to join hands with Thapars to set up the plant. The W. German Government-owned agency, KFW, has preliminarily studied the project for extending their credit. Sybetra of Belgium together with Stamicarbon & Continental Engineering of Holland have been awarded the contract. The total estimated project cost is Rs. 650-700 millions inclusive foreign exchange of about Rs. 22 millions.

[*Chem. Age of India, Anniversary*
No. 21(12) (1970), 1129]

STATISTICS

TABLE 1—EXPORTS OF PETROLEUM PRODUCTS FROM INDIA BY MAJOR COMPANIES DURING 1968

(Quantity: Thousand tonnes)
(Value: Rs. lakhs)

Products	I.O.C.		Burmah-Shell		Esso		Caltex		Total	
	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value
Motor gasoline	47.46	82.43	53.58	143.78	—	—	—	—	101.04	223.21
Bitumen	4.27	15.51	—	—	—	—	—	—	4.27	15.51
Paraffin wax	—	—	2.95	21.11	—	—	—	—	2.95	21.11
Naphtha	125.51	172.36	118.15	144.40	93.93	118.30	54.50	67.03	392.09	502.09
H.S.D.O.	123.57	34.43	—	—	—	—	—	—	23.57	34.43
Furnace oil	23.53	20.34	—	—	—	—	—	—	23.53	20.34
Petroleum coke	10.72	8.58	—	—	—	—	—	—	10.72	18.58
Total	235.06	333.65	174.68	306.29	93.93	118.30	54.50	67.03	558.17	825.27

[Oil Statistics, 7 (4) (1979), 8]

TABLE 2—CENTRAL DUTIES OF EXCISE/CUSTOMS LEVIED ON PETROLEUM PRODUCTS IN INDIA

(As on 30-8-69)

(Rupees per unit)

Products	Unit	At 15°C			At 29.5°C		
		Basic duty	Additional duty	Total	Basic duty	Additional duty	Total
Aviation gasoline 100/130	Kilolitre	620.00	94.75	714.75	609.27	93.11	702.38
Aviation gasoline 115/145	"	620.00	94.75	714.75	608.84	93.05	701.89
Aviation gasoline 73	"	620.00	94.75	714.75	609.09	93.08	702.17
Motor spirit 79	"	620.00	94.75	714.75	609.15	93.08	702.23
Motor spirit 93	"	620.00	94.75	714.75	609.83	93.19	703.02
Aviation turbine fuel	"	205.25	56.35	261.60	202.42	55.57	257.99
Kerosene (superior)	"	205.25	56.35	261.60	202.46	55.58	258.04
Kerosene (inferior)	"	50.90	86.65	137.55	50.28	85.60	135.88
High speed diesel oil	"	461.05	49.60	510.65	455.47	49.00	504.47
Light diesel oil	"	95.55	93.95	189.05	94.47	92.44	186.91
Furnace oil	"	50.75	42.20	92.95	50.24	41.78	92.02
Bitumen straight grade (bulk)	Tonne	15.50	52.25	67.75			
Bitumen straight grade (packed)	"	39.50	52.25	91.75			
Bitumen cutbacks BS/RC	"	36.40	51.50	87.90			

[Oil Statistics, 7 (4) (1970), 9]

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The following papers, communications, etc. have been accepted for publication in TECHNOLOGY Vol. 8 (1971), No. 1, Jan-March.

Papers

ESTIMATION OF WATER-SOLUBLE P_2O_5 IN NORMAL AND TRIPLE SUPERPHOSPHATES USING HIGH FREQUENCY TITRIMETRY AND CONDUCTOMETRY

by A. D. Pandey, K. K. Mallick and A. K. Roy

SIMULTANEOUS ESTIMATION OF IRON AND CHROMIUM IN STAINLESS STEEL BY POLAROGRAPHIC METHOD

By R. M. Bhatnagar, B. N. Singh and A. K. Roy

COMPARISON OF RETENTION AND ARITHMETIC INDICES—THEIR CORRELATIONS AND RELATIVE USEFULNESS IN GAS CHROMATOGRAPHY

by N. C. Saha and G. D. Mitra

CATALYTIC REFORMATIONS OF METHANE

by R. L. Chowdhury, B. P. Sahay, D. K. Mukherjee, N. B. Bhattacharyya and S. P. Sen

EFFECT OF MECHANICAL & HEAT TREATMENT PROCESSES ON PHYSICO-CHEMICAL PROPERTIES OF REFORMATION CATALYST

by S. K. Nath, B. R. Arora, S. C. Chandak, N. C. Ganguli and S. P. Sen

EFFECT OF ADDITIVES ON THE SELF-DISINTEGRATION OF DICALCIUM SILICATE CLINKER

by P. K. Samanta, S. Mukherjee and H. Roy

POLAROGRAPHIC AND ABSORPTION SPECTRAL STUDIES ON THE SYSTEM Cr^{3+} -BIURET

by M. B. Mishra and R. M. Sanyal

MOLYBDENUM RETENTION IN SOILS IN PRESENCE OF FREE IRON OXIDE AND CALCIUM CARBONATE

by S. G. Misra and K. C. Mishra

Short Communications

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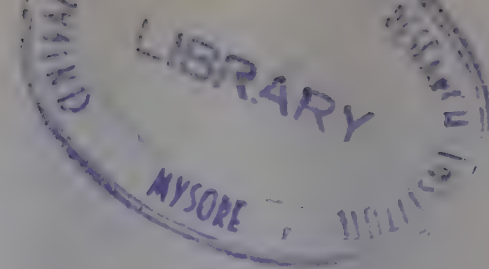
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The New Unified Field Theory of the Universe and Atom

The primordial and eternal problem of understanding the mechanism and true nature of evolution of phenomenal manifestation of the universe from a state of abstract beginning has been explained in this work.

In this work the author explains the application of the postulates of the new Unified Field Theory to the mechanism of continuum of thermodynamic phases along with variation of temperature, development of digits and numbers forming continuum, development of decimal continuum, generation of geometrical configurations of linear, square, cubic and four dimensional continuum, evolution of energy as space in association with atomic matter in the form of periodic continuum, development of energy and matter relationship in equilibrium in the continuum as derived from relationship of magnitudes of squares obtained from square continuum in a plane.

Essential features of the new Theory of Unified Field Continuum have been discussed highlighting the concept of mechanism of change of phase combinations in sequence through critical states, involving maximum of previous and minimum of subsequent; mechanism of transition of fundamental and derived dimensions through a critical state from previous to next. It explains the unified concept of continuum of digits in number in phases of unit, 10, 100, 1000 etc. It explains the nature of variation of intensity of fundamental unit (as one) as well as those of digits in combination in the order of increasing magnitudes of number. It brings out the fundamental significance of unit (as one) and zero (as nil) and the concept of absolute one. It explains the similarity of thermodynamic phase continuum with numerical phase continuum. It also brings out that it is the relative densities of phases in the continuum which counts and not quantity.

It has been shown in the present work that the mechanism of development of continuum of magnitudes as numbers through phases of unit, 10th, 100th, 1000th... is similar to the development of thermodynamic phases including critical states. Concept of fundamental unit of absolute one has been described and mechanism of development of decimal continuum explained. Indistinguishableness of one has been defined.

Mechanism of evolution of square continuum in a plane has been explained. Significance of relationship between side and diagonal of square configuration is explained. There can be two kinds of development of magnitudes of squares in a plane. Criteria for evolution of squares in plane continuum are explained and the concepts of the states of indistinguishableness, distinguishableness and identity are explained with particular reference to criteria adopted in modern statistics. The relationship between numerical continuum and square continuum has been explained:

Concepts of dimension, inertial and non-inertial coordinates and the concept of four dimensional continuum in the approach of the present theory have been discussed. Significance of power in configurations of one, two, three, and four dimensional coordinates have been explained. It has been shown how four dimensional space continuum can be represented in square continuum in a plane.

Mode of presentation of universal wave in terms of numerical magnitudes of squares in continuum of identical square-units in a plane has been explained. Continuum of inertial and non-inertial coordinates have been explained in terms of power of coordinates. Two opposite modes in the development of square continuum in a plane have been discussed and evolution of algebraic formulae representing those have been explained.

Concept of magnitude and its two aspects are discussed and concept of variation of magnitudes in continuum in inertial and non-inertial reference frames as per the present theory has been explained. Significance of roots of squares and roots of number of identical square units in the two aspects of magnitudes have been clarified.

Realisation of velocity of light in its constancy or otherwise in inertial and non-inertial frames has been explained. It has been explained why Michaelson and Morley's experiment cannot detect ether drift.

Radial and orbital development of magnitudes in square continuum have been explained.

Periodic classification of elements and numbers of electrons in orbits have been explained from relationships that are obtained from the mechanism of increasing magnitudes of square evolution in radial and orbital directions as per the present theory. True nature of evolution of matter in association with energy has been explained in terms of square evolution in a plane.

How relative magnitudes of fundamental and derived dimensions (like energy and matter) were determined in square evolution in ancient Indian philosophy has been explained. That approach is identical in significance with the approach in the present theory.

Energy matter relationship in equilibrium in evolution has been explained as per the present theory. That the energy and matter relationship in terms of their respective intensities is in conformity with thermodynamic phase evolution, evolution of numbers and evolution of square continuum have been explained. The mechanism of development of Algebraic formulae incorporating different aspects of energy and matter in combination in space time configurations in terms of square units in plane square continuum have been deduced.

Analysis of characteristics of photon of energy radiation as space has been made and two types of photonic space distinguished: one type which would be in equilibrium with distinguishable atomic matter phase and the other type in which no distinguishable matter would be present. The possibility of a kind of space of indistinguishable photonic state has been predicted. Variation of physical nature of photon in space which would be in equilibrium with varying atomic matter intensities (as atomic number or weight) has been explained and the restricted applicability of the relationship of Einstein's Energy Matter Equivalence has been explained. Einstein's basic premise "what is the necessity of considering a thing which cannot be observed?" has been shown to be incorrect to account for all aspects that are involved in any energy matter manifestation or for that matter, any phenomenon in the inanimate as well as animate domain in the Universe.

Further, it has been shown that the deduction from quantum theory that evolution of atomic numbers of atomic elements in periodic system should be as 2; 8, 8; 18, 18; 32, 32... is incorrect; the present theory shows that this should be as 2, 2; 8, 8; 18, 18; 32, 32;... in which ortho hydrogen, neutron, para-hydrogen and helium make the first group of 4 elements of 2 and 2 and not 2 as in the quantum hypothesis.

INTRODUCTION

This introduction serves to highlight the essentials towards an appreciation and appraisal of the New Unified Field Theory.

The concept of unified field continuum is the central theme involved in the mechanism of evolution of phenomenal manifestation from a state of abstract beginning, e.g. the mechanism of evolution of matter/energy universe from a certain state of origin. Two fundamental questions are involved in this. The first is: "what could be the nature of the state of origin from which the matter/energy phenomenal universe has been evolved and progressively manifested?" And the second question is: "what is the mechanism of evolution of the phenomenal universe and what is the nature of changes that take place during the progress of evolution to a state of equilibrium existence?"

Nature of the State of Origin of Evolution

The first question involves the description of a state which is inconceivable. This state can either be indistinguishable oneness of something or a state of indistinguishable nothingness. A distinguishable phenomenal manifestation would start from such a state.

- 1) अविशेषात् विशेषारम्भः (सांख्यप्रवचनसूत्र)
- 2) अग्रे आसीदेकमेवाद्वितीयम् (बृह-६।२।२-३)

The concept of such a state is beyond description because a state in which nothing exists, except one and in which again nothing is distinguishable, does not lend itself to wordy description. Further, this state, while it can be conceived as consisting of only one and no second constituent and no distinguishableness of the one in it, it can also be imagined as a state in which nothing exists, and there is no distinguishableness and everything is only nil. Thus there can be two definitions of the state which, apparently, are exact opposites. But the concepts involved are equivalent in significance.

This is the concept of the state which forms the basis of and which is at the root of the ancient Indian philosophies on evolution of phenomenal universe, both in the animate and inanimate domain. For example the terms Ekam, Evam, Addvityyam (एकम्, एवम्, अद्वितीयम्)

Nirakar Brahman (निराकार ब्रह्म), Avyaktam (inexpressible) (अव्यक्तम्), Achintaniyam (अचिन्तनीयम्) and other expressions have been used in the different Indian philosophies to express this state. The concept is so abstract that it defies description. On the other hand, unless such a state can be conceived in imagination, the subsequent process of evolution from that state cannot be comprehended. The unified field concept explains the mechanism of transition in evolution as to how absolute concept becomes phenomenal, how formless assumes cognisable form and how abstract becomes concrete, and infinite becomes finite.

Phases of Evolution

For explaining the phases in evolution, the ancient Indian philosophies employed the concepts of phases in sequence, starting from a first abstract state. The evolution occurs in terms of phases (these are the same as thermodynamic phases of modern science) which are, viz.

Vyom	(व्योम)	Nothingness
Tej	(तेज)	Energy (Space)
Marut	(मरुत)	Gas
Aap	(अप)	Liquid
Kshiti	(क्षिति)	Solid.

In the present theory energy is space devoid of distinguishable material phases. Intensity of energy of space is force. Simple instances from available thermodynamic data in modern science explain these states and phases.

The abstract state is equivalent to what we call critical state in thermodynamics. At the critical state, say, in case of gas/liquid, the properties of co-existent liquid and vapour phases merge into oneness, in which their densities, specific volumes, entropies, enthalpies—all properties are identical. There is no property at the critical state which can differentiate the liquid phase from vapour phase. Above the critical state vapour and liquid attain superheated status of oneness, i.e. superheated gas phase. Below the critical state, two distinct or distinguishable phases co-exist in equilibrium: one is condensed like

liquid and the other is non-condensed like vapour.

For the sake of analogy, let us assume that the gas/liquid critical state is the starting state of the subsequent evolution in the direction of decreasing temperature (which is equivalent to energy intensity in the present theory). The phase combinations like vapour/liquid and solid/super-cooled liquid will be the physical nature of phenomenal manifestations in sequence in evolution as the temperature of the phases will progressively decrease, starting from gas/liquid critical state. Below the critical state of gas/liquid, two distinct phases as vapour and liquid will be found to co-exist. As the temperature will progressively decrease further, there should be a next critical state which will be the solid/liquid critical state. In the case of H_2O this state will be somewhere between 0° and $4^\circ C$. This critical state, however, has not been identified as yet. Subsequent to this critical state, in the case of H_2O as the temperature further decreases, the super-cooled liquid decreases in density, and the solid phase (ice) increases in density. This is similar to what happens in vapour/liquid phase in combination above the solid/liquid critical state. In that combination also with decrease of temperature, the vapour phase decreases in density while the liquid phase increases in density. These have been explained in detail in other works.^{1,2}

In order to appreciate the mechanism of evolution, whether it is the inanimate universe or animate universe, the significance of "critical state" must be fully understood. Further, it must be recognised that, in between the two critical states, with reference to a certain reference dimension, say in the above case, temperature or energy intensity, the development of two phases occurs from a previous one and the variation of properties of the two phases, namely vapour and liquid phases, occurs in opposite directions in opposite phases while remaining in equilibrium combination. This is the universal law. When the phenomenal manifestation covers many critical states in sequence, having relevant and permissible phase combinations in the direction of change of energy in intensity, it would generate a unified continuum of manifestations in sequence in evolution.

¹ Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol.* 5(2A), (1968)

² Relativity Analysed in the Light of the Theory of Universal Wave and New Theory of Unified Continuum—*Technol.* 5(3A), (1968).

Significance of Inertial and Non-inertial Coordinates

Einstein's concept of inertial co-ordinate is equivalent to the variation of intensities of two phases in opposite directions in between two consecutive critical states. In the continuum, involving many inertial co-ordinates, which, invariably, has to incorporate different distinct phase combinations in succession, the continuity will be maintained through the various critical states in succession, from previous frame of co-ordinates to next frame in succession, through a critical state involving different phase combinations in succession.

It may be stressed that, for an understanding of the mechanism of evolution and manifestation of the phenomenal universe beginning with a state of oneness, the similarity of the critical states with this state must be fully understood and appreciated.

Unit Universal Wave

Now, suppose the evolution of the universe to have started initially from a state equivalent to oneness at which only energy exists with association of nil material. Let us assume that state as the first critical state. From that state the dimensions energy and matter start in association. As more association of matter significance occurs, while intensity of energy decreases progressively, intensity of matter association increases progressively till a second critical state is reached at which the two attain identity. From this critical state, segregated matter starts in a new phase surrounded by the energy phase (equivalent to vapour phase) till the third critical state at which segregated matter attains maximum intensity, and the energy in the space phase attains least intensity. If we assume that the first critical state starts with infinite intensity of energy dimension called the fundamental in association with nil of matter called the derived dimension, they vary in opposite directions in the wave, starting from the first critical state, passing through a second critical state and ending up in a third critical state at which the fundamental dimension, energy would be reduced in its intensity to nil and the segregated matter intensity in association at that state to infinity. This is the concept of unit wave. The intermediate or second critical state is in between two zones, the first zone being between the first and second critical states and being homogeneous in which matter-energy forms one phase and the second zone being in between the second and third critical states in which energy-matter exists in two distinct phases and is heterogeneous.

The variation of intensity of dimensions in combination like matter and energy in any zone in between two consecutive critical states corresponds to variation along

inertial coordinates with a reference frame like variation of intensity of dimension, like, fundamental. If the entire universe were to be conceived as one unit wave, only then there would be three critical states; first—the critical state from which creation occurs (Srishti) and second—the establishment of equilibrium existence (Sthiti) and third—the state of Pralaya at which intensity of fundamental dimension is destroyed and the derived dimension assumes the property of infinite intensity. These are the three states of Srishti (सृष्टि), Sthiti (स्थिति) and Pralaya (प्रलय) concepts in Indian philosophy. The concept of Triguna in the Indian philosophy referring to Satya, Rajas, and Tama refer to first, second and third critical states respectively. The concept of Trinitti (three laws) refers to variation of properties of three phases in the two zones, which would, for one critical state of gas liquid, be superheated gas phase, vapour phase and liquid phase.

Geometrical configuration of the Unit Wave

It is now necessary to explain the geometrical configuration of the energy matter unit wave involving the dimensions of space and time. The first critical state in which only one exists and nothing else can in imagination be conceived of either as a state of pure energy of infinite magnitude or as the starting state at which the energy is concentrated in an imaginary point of position. Both these states are abstract in concept since both infinity and nil are beyond human comprehension. The concept of unit wave in the present theory starts with energy of infinite intensity, occupying an imaginary point of position, from which the energy, in progressive association with dimension of space, and increasing magnitude of matter, in progressive association with dimension of time, progressively build up the energy-matter universe.

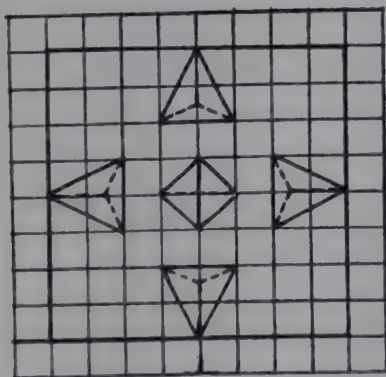


Fig. 1

Starting from a point of position, as the fundamental dimension emanates radially, since it must possess the

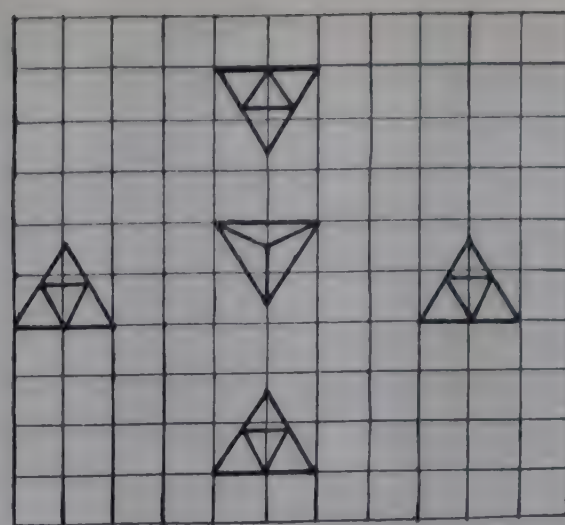


Fig. 2

property of emanation in all directions isotropically, i.e. the emanation from that point of position must occur in most isotropic directions, the configuration of such an evolution must occur towards 4 regular tetrahedral directions. The unique property of this configuration is that, with respect to the starting state of imaginary point of position, the 4 evolved positions are perfectly isotropic. This is one aspect. The other aspect is that, with respect to any evolved position, the other three evolved positions are also isotropic. Thus, between the first imaginary starting state of point of position and the 4 evolved positions of regular tetrahedron is formed one zone, i.e. homogeneous zone of the unit universal wave. After this regular tetrahedron has been evolved the extent of propagation of the wave depends on the intensity of energy and matter in combination and the nature and potentiality of the phase belonging to the first zone. Further evolution will occur from the 4 equilateral triangular faces of this tetrahedron. To these 4 triangular faces, 4 distinct tetrahedra of same magnitude as that of the first can be placed face to face and the apical positions of these 4 regular tetrahedra will form the boundary of the unit universal wave. The 4 apical positions form the third critical state. The 4 positions of the central tetrahedron, at which the central tetrahedron and the 4 outer tetrahedra are in contact, form the second critical state and the centroid of the central tetrahedron, which is the imaginary starting point of position of the emanating dimension, is the first critical state. The configuration, incorporating these aspects, is the geometrical concept of unit universal wave.

Concept of Unified Continuum of Waves in Sequence

If instead of conceiving the entire universe as unit wave, evolution will be conceived in terms of many continuous phases of physical nature, then, between the first critical and the ultimate boundary, there will be

numerous critical states and numerous zones between criticals, having different phases in combination in each zone.

It should be understood that, in the direction of continuous variation of intensity of fundamental, the critical states become the states of transition from one zone to the next succeeding one. No two zones can simultaneously exist. For example, just as in the case of the gas-liquid critical state, vapour phase and segregated liquid phase in combination cannot co-exist in the zone of superheated gas phase; similarly, superheated gas phase cannot exist at the temperature ranges where only liquid and vapour can co-exist.

The author in the various previous works has shown that this very same theory as has been delineated in the concept of universal wave and the new unified field theory was at the very root of development of Indian philosophies. However, though the remnants of those philosophies have been retained and their various applications to different domains of human existence also have been recorded and incorporated in the numerous Shastras including Darshanas, Shruti, Smriti, Vedas, Upanishads, the very fundamental theory which was at the root has been subsequently forgotten. Our real difficulty in going back to the very root lies in the following. No doubt, we have the various works on philosophies and Shastras. But these have undergone considerable distortion owing to lapse of time, since the various authors and their interpretations in subsequent generations lost the significance of the first fundamental, from which all these philosophies and sciences were derived. For example, we are in possession of the digits and numbers. But the very basic theory viz. the concept of unified field, which was at the root of development of these digits and numbers, has been forgotten. For example, what is one? What is the significance of zero? Why there are only nine digits? What is the significance of infinity and what

is the relationship (relativity) between zero, infinity and one? The very basic considerations of all these have been forgotten.

That the discovery of these digits and numbers in ancient times were obtained from an analysis of the mechanism of evolution in 4 directional tetrahedral directions by its conversion into a plane square continuum, has been forgotten. All these and other related aspects have been discussed in the various previous works by the author.

The brief description in the above, has been attempted to describe the nature of geometrical configuration of the unit wave in the universal context, having regular tetrahedral configuration. The ancients fully realised this concept which has been mentioned in some of the previous works^{1,2,3} by the author. However, since an understanding of the universal evolution through a picture in four dimensional context is almost impossible, the ancients had devised means to analyse the universal evolution by translating/converting the tetrahedral evolution to a concept of continuum of squares in a plane wherefrom they had deduced mathematics, algebra, astronomy, trigonometry and other sciences.

It is hoped that this introduction to the basic concepts involved in the present approach will enable the reader to follow and understand the present work.

¹ Evolution of Decimal and Octate System of Numbers and their Magnitudes as Configuration of Space-time Co-ordinates in the Light of the Theory of Universal Wave—*Technol.* 4(1&2), (1967).

² Appraisal of Scientific and Philosophical Concepts in Ancient India in the Light of the Theory of Universal Wave—*Technol.* 5, (1), (1968).

³ Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol.* 5 (2A), (1968.)

CHAPTER 1

The New Unified Field Theory: The Nature of Unified Continuum, Nature of Transition Through Critical States, Thermodynamic Phase Continuum Vs Numerical Continuum (Similarity)

(1) Essential Features of New Theory of Unified Field Continuum

Manifestation of material universe occurs in various phases of physical nature in the background of energy as space. In evolutionary context energy and matter in combination must exist in all manifestations. In the finite universe one cannot exist without the association of the other. But one is previous as cause and the other is the subsequent as effect, which generates the concept of time.

(1) The dimension of energy is symbolically presented in these Works as E and is the cause or is the fundamental dimension whose property is to emanate from a point of position, and that of matter M which is subsequent effect, is derived, whose property is to converge to a point of position.

(2) In manifestations in evolution sum total of relative intensities of E and M remains constant. While acting along constant gradient of energy intensity which is cause and is fundamental (i.e. against constant inertial reference frame* of E) from the highest towards least in space time continuum, matter intensities, which are derived (they are as effects) in their manifestations in association with energy, occurs in sequence through phases as space, gas, liquid and solid. Change of phases occurs from a previous to a subsequent phase in sequence i.e. from previous inertial frame to a subsequent frame in the direction of decreasing energy intensity of space, and takes place at critical equilibrium state of indistinguishableness at which maximum of previous derived changes to minimum of subsequent derived; the previous

phase continues progressively decreasing in intensity while remaining in equilibrium association with the subsequent phase, which is condensed, while the latter increases progressively in intensity towards a maximum at a next critical state.

(3) In the background of progressively decreasing energy intensity in the continuum transition of material phases in association with E, from one indistinguishable previous to a new distinct subsequent, occurs through a critical equilibrium state and establishes the continuity of previous phase to next in sequence through many critical states making a unified continuum.

(4) Direction of decrease of intensity of E from its highest at a point source, causes emanation of space and direction of increase of intensity of matter to its highest is from generated space towards point of position in created space.

(5) Energy emanates space from a position of indistinguishable point source and matter tends towards occupation of distinguishable position of point in created space. Direction of action of energy in space L which is radial and that of matter positions in created space are orbital describing time T. Thus in space time configuration in the continuum, space is radial in action and time is orbital. Energy matter evolution is regular tetrahedral in configuration and is isotropic in action with respect to both E and M.

(6) Space L is the containing dimension of energy E and time T is the containing dimension of matter M. Space L is four directional and time T is three directional.

These are the essence of the theory of unit universal waves and their unified sequential manifestation in space time continuum like phases as space, gas, liquid and solid. This is the fundamental law of inanimate physical nature.

The concept of continuum through a critical equili-

* It is to be noted that these inertial frames have got nothing to do with the inertial or Galilean frames familiar to physics. These are the tetrahedral frames appropriate to each evolutionary stage of the Universal Wave.

brium state from a previous phase to the next, i.e. from a previous inertial frame to a next inertial frame can be illustrated by elementary cases like transition from superheated gas phase through the critical temperature state towards condensed phase liquid in equilibrium with its vapour; the change taking place in the direction of decreasing temperature. Thermodynamic data for any permanent gas above critical temperature* show that when a superheated gas is progressively cooled the density of gas progressively increases. At the critical temperature the superheated gas attains maximum density. If the temperature is lowered further than critical, then two phases co-exist in equilibrium. One is the newly formed condensed phase as liquid and the other phase is the vapour phase in equilibrium with the liquid phase. At the critical state the densities of the vapour phase and the liquid phase are identical. The two phases lose their identity and are indistinguishable. If the temperature is lower than critical, only then there is possibility of existence of two phases. Thermodynamic data again show that as the temperature of liquid, which is condensed phase, is lowered the liquid density progressively increases and the density of the supernatant vapour in equilibrium with condensed phase as liquid progressively decreases. The significance of one inertial frame of reference of any superheated gas phase is that above the critical the rate of decrease of energy intensity of gas which is same as temperature gradient is in association with the rate of increase of density of the gas in the same phase which is matter intensity gradient. They vary in opposite directions in this particular inertial frame of superheated gas above critical.

In the state below this critical with decrease of temperature, i.e. decrease of energy intensity, the vapour phase decreases in its density whereas the associated condensed phase liquid in equilibrium with it progressively increases in density; thus they also vary in opposite directions. Through the critical the change occurs from one previous inertial frame to subsequent another frame. Modern thermodynamics has realised one critical state between, namely liquid vapour and superheated gas above critical. But there are other critical states which also should exist between say liquid superheated and supercooled liquid with respect to that critical state in equilibrium with solid phase. This solid-liquid critical phase has not been distinctly realised as yet. In one of

the works*, from the available thermodynamic data evidence of existence of this critical state has been explained.

Another elementary case which may be considered to illustrate the concept of continuum is that of progressive cooling of a superheated solution of a salt in solvent. The salt and the solvent above a certain temperature can only exist in an indistinguishable phase quite unlike the crystalline salt. As the temperature decreases through a certain temperature which can be called critical, the solid salt phase appears in equilibrium with mother liquor having a certain concentration which is the function of the temperature. With progressive lowering of the temperature the mother liquor progressively decreases in concentration of the salt whereas solid phase increases in density of separated crystals.

In both the illustrations, material gas and space in one case and salt and solvent in another case, as the temperature decreases the intensities (i.e. the quantities per spatial unit) of the two vary in opposite direction. It is the intensity which counts and which varies maintaining the constancy of their sum. This rule or law does not apply to the quantities themselves. Most important aspect is the change of the dimensions at the critical i.e. change of intensities of the dimensions through the critical, at which in the phase above the critical assumes minimum intensity of one dimension and maximum of the other in their relative intensities. At the critical, one is least and the other is maximum both remaining indistinguishable. Below the critical distinct phases appear; one as condensed phase in the background of another phase say vapour or mother liquor in which the two dimensions are in distinguishable phases; but the matter concentration in the phase pertaining to condensed phase progressively increases with lowering of temperature. Though the condensed and the depleted phase start with equal intensity at the critical, the intensity in the depleted phase progressively decreases in the same direction of decrease of temperature; whereas in the condensed phase the intensity progressively increases, i.e. intensities of depleted phase and the condensed phase vary in opposite directions. If one would take only the condensed phase then with intensity of energy variation is towards decrease and the intensity of matter variation is towards increase. The transition through critical from one previous to next thus occurs through maximum of previous condensed

* Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol.* 5 (2A), (1968)

* Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol.* 5 (2A), (1968).

and minimum of next condensed. The background reference co-ordinate of temperature gradient however retains the same inertial frame. If instead of one critical several criticals are involved in sequence in order to generate a continuum of several phases, then the same manner of transition will be repeated at all the critical states in sequence while transitting from one previous condensed to next condensed through the maximum of previous to minimum of next. This is the fundamental law of nature.

(2) Mechanism of Change or Transition at a Critical state: Mechanism of Transition of Fundamental and Derived Dimensions at a Critical State from a Previous to Next Phase

The postulates of the fundamental law would thus be as follows:

Along the intensity gradient of fundamental (in order of decreasing magnitude of intensity) the following changes can be discerned at a critical state:

Least magnitude of first fundamental of the first phase changes to maximum of second fundamental of the second or subsequent phase (in continuity as homogeneous).

Maximum of first condensed phase changes to least of second condensed phase (heterogeneous).

Maximum of first condensed phase changes to maximum of second fundamental of second phase (in continuity).

Least of first fundamental changes to least of second condensed phase (heterogeneous).

These are the 4 changes that occur at a critical state. This can be illustrated by taking any critical state of any entity between superheated gas, liquid, and depleted vapour in equilibrium at the critical state. With progressive reduction of temperature of space as the first fundamental, at the critical state, the density of condensed phase as gas is maximum for that superheated phase. At the critical, the superheated gas density changes to vapour density at its maximum in equilibrium with new phase liquid of least density, whence subsequently vapour density decreases and liquid density increases with decrease of temperature. The maximum superheated gas phase density at critical, changes to least density of liquid phase at the critical. Superheated liquid phase (second phase) is subsequent to superheated gas phase. The least temperature of superheated gas at the critical changes to least density of condensed phase as liquid. These changes at critical are applicable to all liquid, vapour and gas equilibrium at their corresponding critical

states. The same is true for liquid-solid critical states also. The case of H_2O at its solid-liquid critical equilibrium state has been explained elsewhere.* Another illustration also has been presented in the same work in the periodic classification of elements. The critical states here are inert gas states. The transition occurs at that state from least intensity of positive properties of previous element to highest intensity of positive properties of element in the next series. The maximum intensity of negative properties of elements in the previous series changes to least intensity of negative properties of elements in the next series.

It will be shown in subsequent sections in the present work that the same principle is applicable in the evolution of numbers in which the intensity of the digits and intensity of fundamental unit, change from previous to next through critical states of 0, 10, 100 etc.

(3) All Continua are Similar in Mechanism: Unified Continuum of Digits in Number as per the New Theory of Unified Continuum

(1) E and M occur in combination in which their intensities vary in opposite directions such that sum total of their intensities remains constant in the wave in the unified continuum.

(2) Matter manifestation occurs in association with E as different phases, such as solid, liquid, gas, space etc. Space is energy; Matter is position describing time in created space by E in association with M.

(3) E is fundamental and cause and M is subsequent derived as effect.

(4) Manifestation of E and M in progressive evolution occurs in sequence from inf. E, through matter phases in association with energy in succession of phases as space, gas, liquid, solid in the direction of decreasing energy intensity and increasing matter intensities of matter phases per position (momentum) in sequence.

(5) Change of one phase to another occurs through critical states at which transition occurs through maximum of previous (super intensified) condensed phase and minimum of subsequent new (condensed) phase surrounded by progressively depleting previous phase in continuity. Inertial continuum of rate of increase or decrease of intensities in the three states in the direction of decreasing energy intensity is illustrated briefly in the following mechanism which has been explained before.

* Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol.* 5 (2A), (1968).

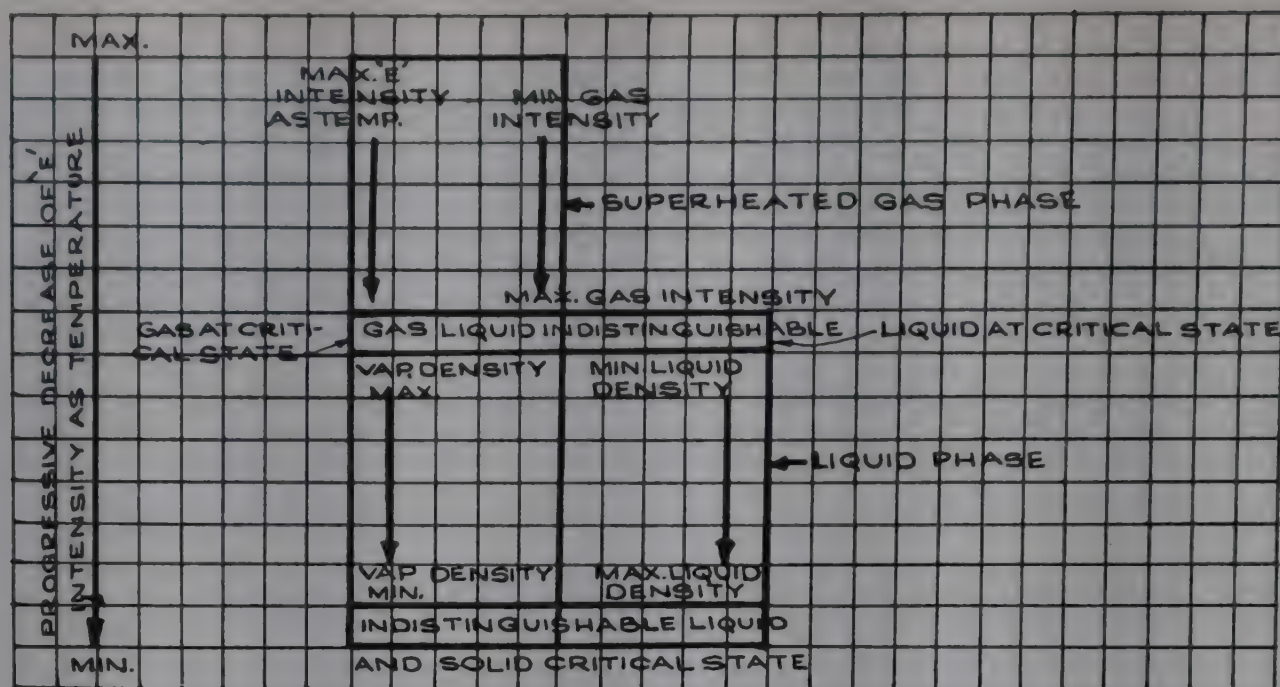


Fig. 1

(4) Nature of Intensity Variation of Fundamental Unit and Digits in Combination as Numbers of Increasing Magnitude

The nature of intensity variation of the phases in a continuum obviously was realised in the past also by the ancients which led to the evolution of the concept of fundamental unit, zero, digits, and numbers in the increasing order of magnitudes of numbers and their relative intensities in phases of unit state, tenth, hundredth, thousandth and so on (which are inertial states as phases) like variation of intensities of gas, liquid and solid phases and their transition through critical states.

The application of the postulates of this Fundamental Law of Nature has been made in the various previous works on the subject by the author.^{1,2} It has been applied to explain the changes of thermodynamic properties of phases from gas to liquid, liquid to solid taking specific cases in the direction of decreasing temperature which is energy intensity gradient of space in the present theory. It also explains the classification of matter elements in periodic system in the direction of increasing atomic weights which is matter intensity gradient in the present theory. The principle of evolution of numbers in the decimal system has also been explained in one of the

treatises.³ In those, however, for the sake of illustration digits were assumed as intensities themselves for both previous and subsequent i.e. for fundamental and derived such as:

Fundamental cause	9 8 7 6 5 4 3 2 1 0	} in combination
Subsequent effect	0 1 2 3 4 5 6 7 8 9	

Sum total of intensities remains constant as 10 in combination but their individual intensities vary in opposite direction. Actual significance of digits however is not revealed in this presentation. Digits should be numbers and not intensities. Variations of intensities of digits in combination of numbers should be discerned from calculation.

The variation of intensities of digits of one previous and one next would be exemplified by the following: Like gas, liquid and solid a continuum can be represented by numerals.

	Previous	Next	Combined sum total number
	1	0	1
	1	1	2
	1	2	3
First continuum:	1	3	4
	1	4	5
			... Critical state.

¹ Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol.* 5 (2A), (1968).

² Relativity Analysed in the Light of the Theory of Universal Wave and New Theory of Unified Continuum—*Technol.* 5 (3A), (1968).

³ Evolution of Decimal and Octate system of number & their magnitudes as configuration of spaces time coordinates in the light of the Theory of Universal Wave.—*Technol.* 3(3), (1966).

	<i>Previous</i>	<i>Next</i>	<i>Combined sum total number</i>
Second continuum	5	1	6
	5	2	7
	5	3	8
	5	4	9

The intensities of the fundamental unit and the digits in the first continuum in their total magnitudes are as follows:

	<i>Intensity of previous</i>	<i>Intensity of next</i>
	1/1	0/1
	1/2	1/2
	1/3	2/3
	1/4	3/4
	1/5	4/5

Though the sum, as number, increases as 1, 2, 3, 4, 5 the sum total of the two, belonging to previous and next, in terms of their intensities constituting them is constant as 1 for example in the first continuum:

<i>Previous</i>	<i>Next</i>
1/1 +	0/1 =1
1/2 +	1/2 =1
1/3 +	2/3 =1
1/4 +	3/4 =1
1/5 +	4/5 =1

Similarly in the Second continuum:

<i>Previous</i>	<i>Next</i>
$\frac{5}{5+1} +$	$\frac{1}{5+1} =1$
$\frac{5}{5+2} +$	$\frac{2}{5+2} =1$
$\frac{5}{5+3} +$	$\frac{3}{5+3} =1$
$\frac{5}{5+4} +$	$\frac{4}{5+4} =1$

In Fig. 3 numerical presentation involving 9 digits instead of 5 through critical states would reveal the

same significance of transition in the continuum.

The most important and significant aspect however lies in the realisation of the nature of variation of various magnitudes of the phases as inertial states in which the two vary in opposite directions in the continuum in terms of their intensities. In the case of energy and matter as gas and liquid the reference co-ordinate is energy intensity of space as temperature, perception of which is however, revealed through matter. Its gradient remains constant. But the derived dimension as condensed phase separates out starting with least density at the first critical, varies in one inertial frame to maximum towards second critical and after transition through second critical, second condensed phase starts with least intensity of that phase which progressively rises to maximum through second inertial frame towards third critical state. In the evolution of numbers these aspects must be incorporated. Like temperature as intensity of fundamental E, in numerical evolution ultimate reference is to variation of intensity of fundamental unit. Therefore, the concept of highest and least intensities of the fundamental and least and highest of the derived in combination in succession has to be understood in full. We are thus confronted with the question—what is the highest and least intensity of the fundamental and what is the least and highest of the derived ones in combination while the two would remain in equilibrium combination in the direction of increasing magnitudes of digits as numbers? The concepts of 0, 1 and 9 have to be analysed in this context. In our inherited conventionally accepted principle of digits, there are only 9 finites and 0. That it is not more than 9 derived in a particular inertial frame of reference co-ordinate in the overall continuum of intensity of fundamental unit of one has been illustrated from the configuration of the unit universal wave as has been propounded in the previous works.

Taking the configuration of the universal wave as one unit, it starts with a situation of an imaginary point source of position of fundamental where no second derived dimension exists in association (whose intensity is nil in that combination). It was only one fundamental with no second associated. The concept is identical with Ekam, Evam, Advitiyam (एकम्, एवम्, अद्वितीयम्).

This first point source of position occupying the fundamental, contains no second derived magnitude which is only nil and which can be ascribed as zero. Thus the point source is an association of fundamental 1 with zero of derived. Here, for the sake of simplicity assume that both these references are to intensities of the two dimensions.

Fundamental	$\frac{\text{All}}{\text{One unit}}$	$=\alpha$
	$\frac{\text{Nil}}{\text{All in one unit}}$	$=0$

Fundamental emanates from point source and the tendency of the derived is convergence towards point of position. Now if a point source of fundamental with association of nil of derived has to emanate in which the derived will increase in intensity, then the intensity of fundamental from its highest at point source would progressively decrease in intensity in combination with derived whose intensity will progressively increase starting from zero in combination. Both, however, remain in indistinguishable form in this particular frame of reference. The most isotropic emanation with respect to both fundamental and derived is regular tetrahedral in which the emanated regular tetrahedral apical positions with respect to the central point source of fundamental are all identical and with respect to any emanated apical position the other three emanated apical positions of derived are also identical. This unique condition can only be satisfied if the emanation occurs in sequence from one fundamental point source towards points of position of derived in a regular tetrahedral form in which the 4 positions of tetrahedron with respect to its centre are identical and with respect to any of the 4 evolved positions the other three are also identical. But the direction of first is radial and the directions of second in this case are orbital. Thus the fundamental maintains 4 radial directional isotropy and the derived maintains 3 orbital directional isotropy. Both configurations could be regular tetrahedron.

The configuration of the universal wave following regular tetrahedral arrangement consists of one central of 4 evolved positions and including the centre the number is 5. Within this tetrahedron there is homogeneous zone, outside the central tetrahedron 4 distinct tetrahedra are associated with 4 triangular faces of the central tetrahedron which makes tetrahedral boundary of 4 positions, namely, the 4 apical positions of the 4 outer tetrahedra. The zone between the 4 triangular faces of central and the 4 outer apical positions is heterogeneous as it contains 4 distinct tetrahedra. In this configuration one encounters the following aspects. In the central tetrahedron 4 evolved positions (this is one phase i.e. say position phases) plus the centre make total of 5 and 4 outer tetrahedra (which is new phase i.e. configuration phase) making the sum total of $5+4=9$. These are the 9 aspects in one complete unit of universal wave. When the wave is completed before it will start

a new evolution it has to pass through a critical state where the digit 9 of the first unit wave constitutes one complete wave of 9 with which centre of the second tetrahedron making total of $9+1$ association of second in this state is nil. This is the number 10, which becomes the cause of the next evolution. The phase of change from 1 to 9 is in distinguishable phase, 0 and 10 states are indistinguishable states.

Cause States are Indistinguishable (these may be called abstract); Effect Phases are Distinguishables (these may be called concrete or objective or perceptible).

It should be realised from the configuration of this unit wave as described in the above that the 4 positions of the central tetrahedron are also regular tetrahedron and the 4 apical positions of the 4 outer tetrahedra also make a regular tetrahedron but the magnitude of size of the latter is bigger than the central. Further evolution of the regular tetrahedral configuration will occur from the 4 triangular faces of the bigger tetrahedron and with all the implications that are present in the first unit tetrahedral wave. The significance lies in the fact that in the central tetrahedron all the space in it is filled and no vacant space is left. But in the next series of 4 tetrahedra, space is left between the tetrahedra. Similarly for the third series of 4 tetrahedra there will be further more vacant spaces left.

(5) Concepts of Zero and 1

1 represents whole of previous and 0 represents nil of the next in association with the previous one. We have to analyse what is the significance of 1 and what is the significance of nil or zero. 1 represents a digit in which intensity of dimension which is previous is maximum or infinity and 0 represents one in which the intensity of next in association with it is nil. What does it signify? When a thing is one and only one, no second is associated, then in that one, the intensity of that one is infinity. In that one when the second is not present then the intensity of the second in that state is nil and its numerical magnitude can be symbolically written as 0.

We have to understand clearly the definitions of 1 and 0. If a thing is infinitely pure and which is not discernible from even any configuration of individual unit of that one, i.e. which is indistinguishable, then with respect to that one its picture is indistinguishable since all of it is absolutely identical. Since no second is discernible such a thing is not conceivable in comprehension. It can be an imagination only. As soon as a second appears in that indistinguishable one, however less magnitude of that second may be, so long as it

remains finite, two distinguishables are present in that combination. Thus absolute one becomes finite or real in two. In this combination intensity of the first becomes less than infinity and becomes finite. Association of finite second is there and therefore infinity of first will be reduced to the finite highest due to this. The intensity of the second becomes finite least which is higher than the magnitude of its nil intensity in the previous state where the magnitude of intensity of first was infinity. Thus infinity and nil are perfect opposites, and both are indistinguishables.

The transition of one phase to next through a critical state from infinity of the previous and nil of the next has to be appreciated and realised in this context of analysis. In place of indistinguishableness or identity of one thing, one can use the concept of purity or its intensity. But when a second is added to indistinguishable one, its intensity in combination can vary from nil towards a maximum value in one inertial frame of reference in which simultaneously the first varies from its highest intensity towards a minimum value in that inertial frame both remaining in one phase.

Herein lies the significance of the postulate that in the indistinguishable background of oneness of a cause or fundamental, the distinguishable one appears as subsequent as derived which makes the transition of previous through a critical state to a subsequent forming a sequence in continuity: the transition occurs from maximum of the previous indistinguishable towards minimum of subsequent distinguishable making the continuity of the continuum. Since this significant aspect of transition through any critical is identical and repetitive for all changes through critical states, the mechanism of increase of magnitudes of digits and the formation of the numbers generating a continuum of increasing magnitudes, finds explanation arising out of this unique law.

We give an elementary example to illustrate this. If 1 is the property of a pure thing to start with, unassociated with any other in any manner, the property 1 of the thing remains same as 1 be it called purity or intensity or any intensive property say relativity which is one. But when a second thing is associated the purity of first must be progressively reduced in the combination.

Purity or intensity of first would be equal to

Magnitude of first thing

magnitude of first thing + magnitude of second thing.

When the first is in combination with second in this relative proportion, say whole or one of first and zero

or nil of second, the intensity of first in the combination would be

$$\frac{1 \text{ of first}}{1 \text{ of first} + \text{zero of second}} = 1/1 = 1$$

and intensity of second in the combination would be

$$\frac{\text{zero of second}}{1 \text{ of first} + \text{zero of second}} = \text{Zero}/1 = \text{nil}.$$

Presenting symbolically: if the first is symbolised as 0 and the second as θ the following deductions would be relevant.

The intensity of first could be expressed as $\frac{0}{0+\theta}$;

this is less than when the first was alone and pure namely

when it was $\frac{0}{0+\text{nothing}}$

Similarly intensity of second in the same combination

is $\frac{\theta}{0+\theta}$. This is greater than the second's intensity in the

previous case when first was pure which had nil of

second namely $\frac{\text{nil}}{0+\text{nil}}$. If two second things are added to

the pure first, then intensity of the first would be further

reduced to $\frac{0}{0+\theta+\theta}$, when the intensity of second

would increase to $\frac{\theta+\theta}{0+\theta+\theta}$.

Further addition of seconds to the first would further decrease intensity of the first in the combination and increase further the intensity of second in the combination. This process of progressive decrease of intensity of first and increase of second will go on with progressive increase of second in the combination. The sum of the two intensities at every stage however remains constant as 1.

Let us now analyse the continuum of magnitudes as would be developed by first and second in terms of their quantitative numerical significance.

If in the continuum representations would be made by cognisable quantitative symbols, like digits and numbers which have now become cognisable, say 1' for the first and 0, 1, 2, 3, 4, 5, 6 for the second in the background of first remaining constant, the second varying,

the inertial frame of progressively increasing combined magnitude would be represented as:

<i>First</i>	<i>Second</i>
1'	0
1'	1
1'	2
1'	3
1'	4
and so on	

Now suppose the combination is such that the first and second in their combination are indistinguishable and inseparable from one another then the combination would be represented as:

1 for 1'	+0
2 for 1'	+1
3 for 1'	+2
4 for 1'	+3
5 for 1'	+4
and so on.	

In this inertial frame, the progressively decreasing intensity of first would be represented as $\frac{1}{4}$ $\frac{1}{2}$ $\frac{1}{3}$ $\frac{1}{4}$ and $\frac{1}{5}$ and the progressively increasing intensities of the second would be as 0/1, 1/2, 2/3, 3/4, 4/5 etc.

Now suppose to this state third thing is associated in the combination, then presentation of the inertial frame would be as follows:

	<i>First</i>	<i>Second</i>
First inertial frame	1'	0
of first and second	1'	1
in combination	1'	2
	1'	3
	1'	4
	<i>Combined first+second</i>	<i>third</i>
The next inertial	5	0
frame after asso-	5	1
ciation of the third	5	2
	5	3
	5	4

In which intensity of 5 (first+second) progressively decreases as 5/5, 5/6, 5/7, 5/8, and 5/9 and intensity of third increases in the combination as: 0/5, 1/6, 2/7, 3/8, 4/9.

The above analysis, though very elementary, gives

the basis of evolution of numbers and quantities and the intensities of fundamental unit and digits in the first, second, third etc. phases in the increasing magnitudes of numbers in the continuum.

When the above is interpreted to explain the intensity states in terms of phases in sequences as first phase, (figs. 2 and 3), second phase, third phase, fourth phase etc., the following become relevant. In the background of indistinguishable first, second distinguishable develops with minimum intensity rising to maximum with intensity of first decreasing. In the background association of indistinguishable first plus second in combination when they arrive at their critical limits of minimum and maximum respectively, the third distinguishable appears and develops from minimum intensity and progressively increases to maximum, while the intensity of combined phase (first+second) decreases. In the next continuum, subsequently, in the indistinguishable background of combination of (first+second+third) where first is further reduced and second also is reduced and third rose to maximum, the 4th distinguishable starts with minimum in the next continuum rising to maximum in intensity while first+second+third decreases. This process continues and establishes the continuity of the different inertial frames in sequence making unified continuum of phases in succession.

This is the essence of the theory of universal wave and the mechanism not only of a unit frame (one inertial co-ordinate) but also of different frames in combination in establishing continuity of many different inertial co-ordinates in succession leading to unified continuity of the continuum as propounded in the new theory of unified continuum of different inertial co-ordinates in succession which has been applied to explain different thermodynamic phases as space, gas, liquid and solid as per their intensities in succession with respect to decreasing energy intensity realised as temperature through medium of matter (not pure energy as such). This also explains significance of the atomic elements in their arrangement in periodic system forming continuum of realised intensities in terms of their atomic weights and numbers and atomic radii.

Most significant aspect of the unified continuum is that the continuity from previous (one inertial coordinate) to next must be through a state *which is critical* at which the intensity of indistinguishable previous fundamental reaches from maximum to a minimum limit and a distinguishable derived in combination starting with minimum rises in intensity to a maximum value and also from that state the two in combination as indistinguishable continues to reduce in their own intensities

while from that state a third subsequent develops starting with minimum rising to maximum.

Another important aspect which we have to discern is; what is indistinguishable and what is distinguishable—with respect to what and whom?

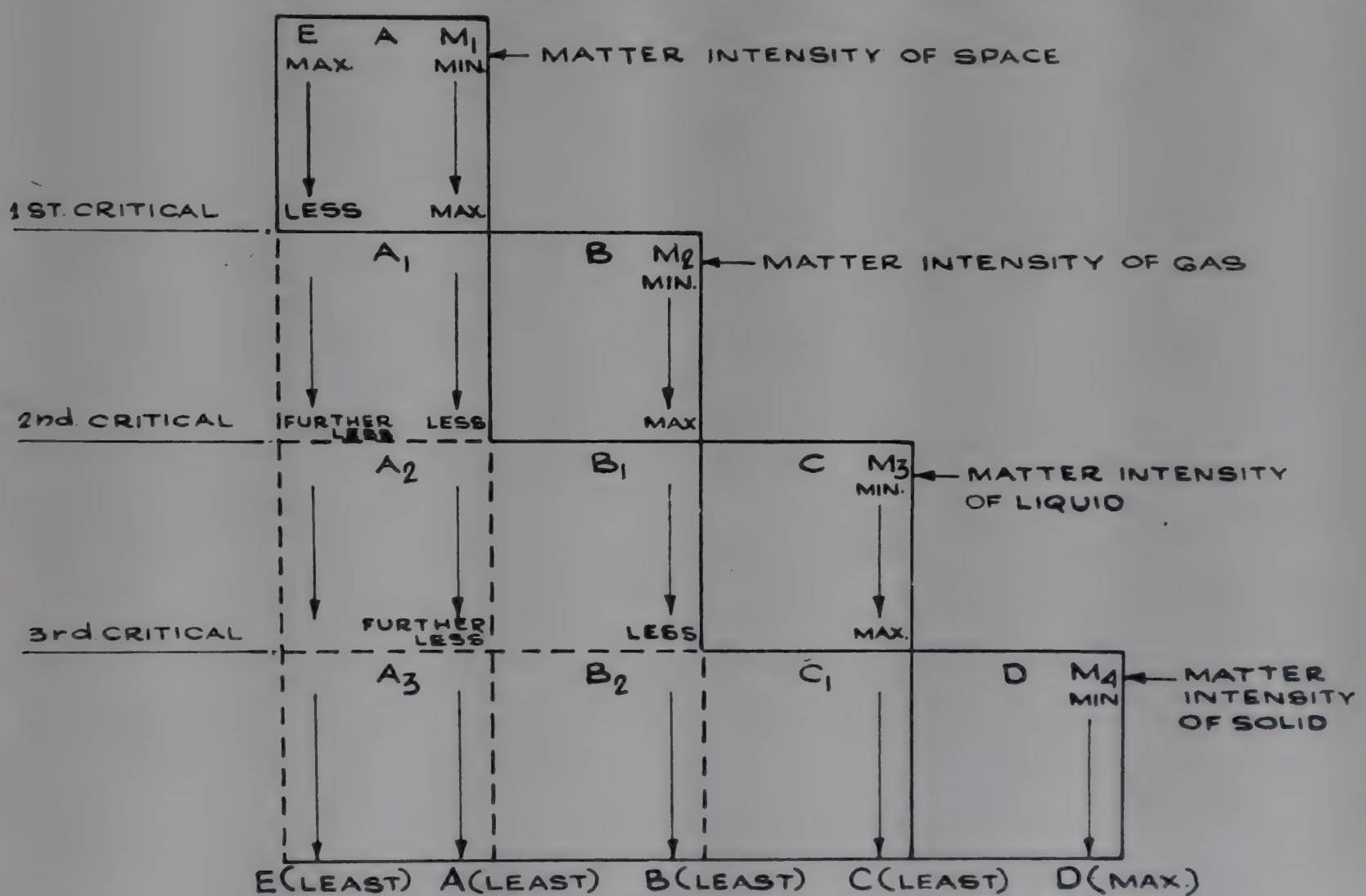
With respect to distinguishable liquid, superheated gas is indistinguishable, and with respect to distinguishable solid, superheated liquid is indistinguishable while in association in the continuum (gradient) of decreasing temperature. This aspect will be further discussed in a subsequent section.

(6) Similarity of Thermodynamic Phase Continuum with Numerical Phase Continuum

Though it may be repetitive we would further discuss the details of nature of the concept of unified field con-

tinuum as has been shown in figs. 2, 3, 4 and 5.

In fig. 2, the change of phases starts from energy E as space through subsequent phases as gas, liquid, solid. In the first compartment A, in which energy E and its opposite M_1 as some materialistic property (say force) of space vary in opposite direction in combination in one inertial frame of reference co-ordinate. In A of fig. 2 energy intensity of space starting from maximum, decreases in combination with matter properties of space M_1 which progressively increases from minimum towards maximum at the first critical state. Subsequent to first critical state the phases A_1 and B would be co-existent. B is condensed phase as gas surrounded by space A_1 of progressively depleting energy intensity of space. A_1 starts with maximum at first critical which progressively decreases towards the second critical. After



- A—Superintensified Space Phase with Respect to E
- A_1 —Depleted Space Phase with Respect to E
- A_2 —Further Depleted Space Phase with Respect to E
- A_3 —Maximum Depleted Space Phase with Respect to E
- B—New Condensed Phase as Gas with Depleted Space
- B_1 —Depleted Gas Phase as Vapour
- B_2 —Further Depleted Gas Phase as Vapour
- C—New Condensed Phase as Liquid with Depleted Gas Phase
- C_1 —Depleted Liquid Phase
- D—New Condensed Phase as Solid with Depleted Liquid Phase

Fig. 2—Variation of Intensities of E and M of Different Phases in the Continuum

INERTIAL COORDINATE 1 to 10	1	0	CRITICAL STATE OF 1					
	1	1						
	1	2						
	1	3						
	1	4						
	1	5						
	1	6						
	1	7						
	1	8						
	1	9	10	0	CRITICAL STATE OF 10			
INERTIAL COORDINATE 10 to 100		10	10					
		10	20					
		10	30					
		10	40					
		10	50					
		10	60					
		10	70					
		10	80					
	10	90	100	0	CRITICAL STATE OF 100			
INERTIAL COORDINATE 100 to 1000			100	100				
			100	200				
			100	300				
			100	400				
			100	500				
			100	600				
			100	700				
			100	800				
		100	900	1000	0	CRITICAL STATE OF 1000		
INERTIAL COORDINATE 1000 to 10000				1000	1000			
				1000	2000			
				1000	3000			
				1000	4000			
				1000	5000			
				1000	6000			
				1000	7000			
				1000	8000			
			1000	9000	10000	0		
							-	-
							-	-

Fig. 3—Continuous Variation of Magnitudes of Numbers Through Various Phases and Critical States of Unit 10, 100, 1000 etc.

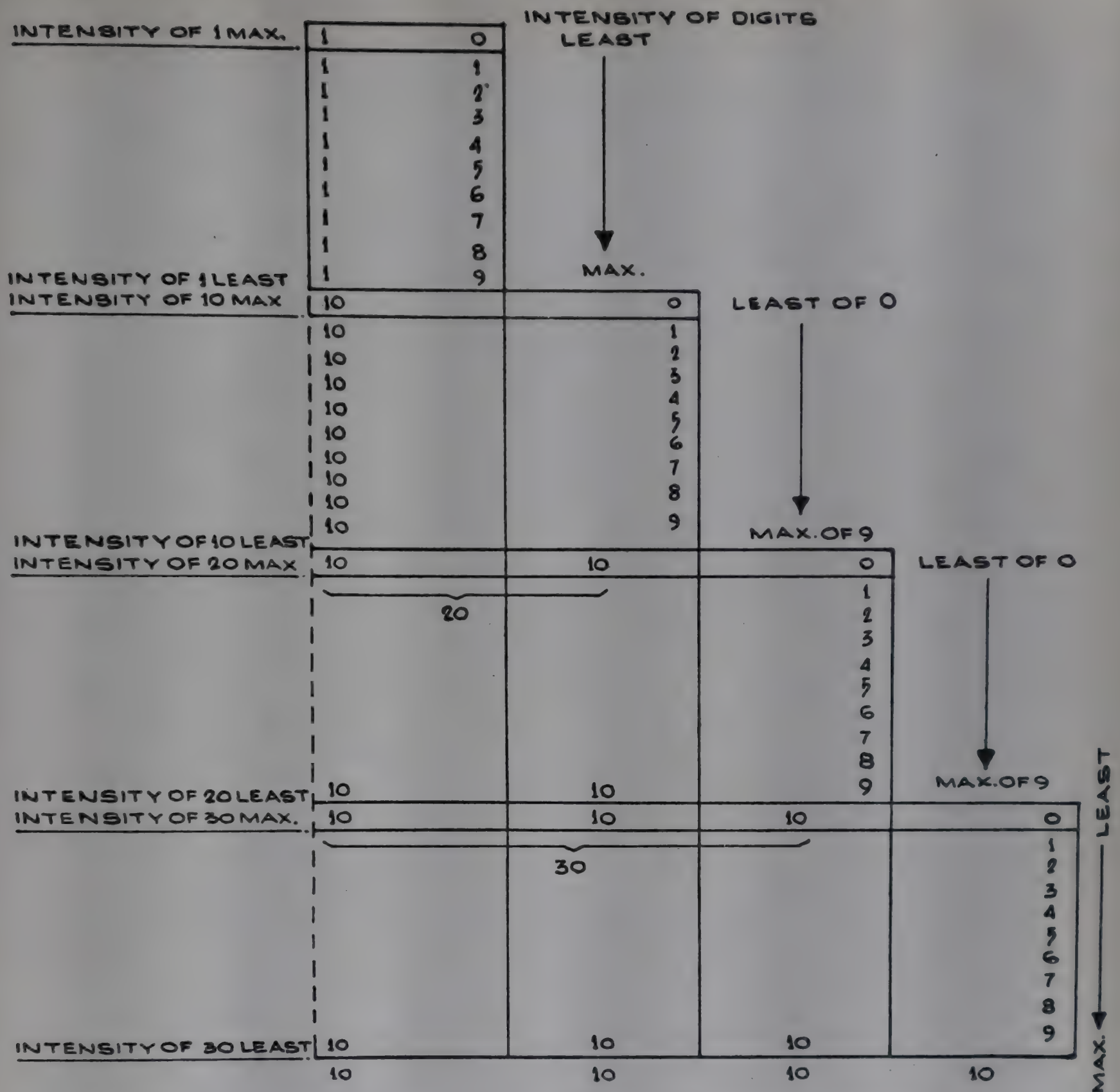


Fig. 4—Variation of Intensities of 1 and the Digits in the Continuum of Increasing Magnitude in Different Phases as Unitth, Tenth etc.

the first critical the new condensed phase gas whose matter property is M_2 which is matter intensity or density, progressively increases from minimum to maximum towards second critical. From second critical state a new phase C of liquid appears whose matter intensity as M_3 starting with minimum arrives at maximum at third critical stage. At second critical state the phase B reaches its maximum. From second critical

the vapour phase B_1 progressively decreases in intensity towards third critical. At the third critical the phase D of solid appears, the matter intensity of which starting with minimum at the third critical progressively rises to maximum at the 4th critical whereas in continuity of previous phase C, from third critical state the phase C_1 (as super cooled liquid phase) progressively decreases in intensity from third critical to least at 4th critical

while in association with progressively increasing intensity of solid phase to maximum in D towards 4th critical.

Finally at the least energy intensity at 4th state the space, whose intensity was highest to start with reduces through stages A_1 A_2 A_3 and reaches least intensity at the 4th state, where the gas phase from B_1 to B_2 reaches least intensity, at 4th state the liquid phase C_1 reaches least intensity whereas the last phase, solid, in the sequence in the continuum reaches maximum in intensity at the 4th state.

(7) Relative Densities of Phases (Archimedes' Principle)

The specific properties which characterise different phases as solid, liquid, gas, space etc. and their progressive transition from one phase to another in sequence in the direction of increase or decrease of energy intensity as temperature are determined by the intensive properties of the phases such as density or pressure. Every one knows that, of all the phases density of solid is highest, next lower is liquid phase, and then gas and the lightest is space (which is considered as vacuum according to modern science, but according to the present theory, it is energy and not true vacuum, and the space has least density in terms of intensity of material property of space as is perceived of gas, liquid and solid).

Archimedes discovered that certain unit volume of solid when weighed in liquid medium loses in weight from its weight in air equivalent to the weight of equal volume of the liquid. A solid, thus, when weighed in air, has its weight per unit volume higher than that of its weight in liquid. If the weight of the solid per unit volume in air which is a gaseous medium, would be compared to its weight in so called vacuum, i.e. only space medium devoid of any material gases, it would be found that the weight of solid per unit volume of space as vacuum would be higher than the weight per unit volume of the solid in gas phase. Similarly, it can be extrapolated that weight per unit volume of solid in solid phase medium (if it were possible) will be zero.

If the intensity or density of the different phases as medium in which the relative specific weights of solid body would be determined, the sum total of the intensities of the solid body and the phase would be constant.

Space phase medium has least density, the solid in this medium has highest weight per unit volume. Gas phase has higher density than space phase. In gas phase medium weight of the solid per unit volume is less than its specific weight in the space phase. Similarly in liquid phase weight per unit volume of solid is less than that of its specific weight in gas phase. Similarly in solid phase medium if the specific weight of solid could be

determined it would be least and same as that of the medium itself. It thus follows that the specific weights of the solid body in different phases would be different, as well as the phases themselves have different specific weights, but their sum total in association in all the phases can be constant.

	Specific weights of phase medium	Specific weight of solid body
Space	a_1	a_2
Gas	b_1	b_2
Liquid	c_1	c_2
Solid	d_1	d_2

Suppose a_1, b_1, c_1, d_1 are specific weights of the different media, space, gas, liquid, solid respectively. The specific weights of solid body if would be determined in these different media and would be a_2, b_2, c_2, d_2 , their relative intensities would be $\frac{a_1}{\text{unit vol.}}$ and $\frac{a_2}{\text{unit vol.}}$ in space

phase, $b_1/1$ and $b_2/1$ in gas phase, $c_1/1$ and $c_2/1$ in liquid phase, and $d_1/1$ and $d_2/1$ in solid phase. If the magnitude of unit volume is same in all the phases, then each of $a_1+a_2, b_1+b_2, c_1+c_2$ and d_1+d_2 will have same value. If instead of a_1, b_1, c_1, d_1 and a_2, b_2, c_2, d_2 , absolute specific weights of the media and the solid body would be represented progressively in terms of increasing magnitudes and if the solid body possess identical specific weights as that of solid phase, say a , then as has been shown in the following the sum total of the specific weights of the solid body and the solid media in the solid phase is $a+a$. The specific weight of the liquid media $a-1$ and the specific weight of the solid in liquid medium is $a+1$, their sum total is $a+a$; similarly for gas and space media their sum total will be $a+a$ for both.

	Specific weight of medium	Specific weight of solid body in the medium
Space	$a-3$	$a+3$
Gas	$a-2$	$a+2$
Liquid	$a-1$	$a+1$
Solid	a	a

The matter and energy dimensions in combination in terms of their intensities which has been adopted in the theory of universal wave and in the new theory of unified field continuum of different phases, correspond to the same principle as has been explained just now by this elementary example. The two opposite dimensions vary in their combination in terms of their intensities in

opposite direction. This generates the general inertial frame of reference in the continuum. But change of one previous phase to another subsequent occurs through a critical state where the intensity variation takes place also in opposite directions which has been explained in the earlier sections.

CHAPTER 2

Continuum of Numbers and Decimal Continuum

(1) Continuum of Numbers

The numerical continuum expressed in figs. 3 and 4 are similar. In fig. 3 the numerical continuum in sequence of phases of 1st, 10th, 100th, 1000th and their progressive transition through their various critical states have been shown. In fig. 4 the transition has been elaborated in phases of unit, 10, 20, 30 etc.

Energy as space in the phenomenal universe must exist anywhere and everywhere and manifest itself in different phases in combination with matter giving rise to their appearance as solid, liquid, gas etc. The property of energy as fundamental is emanation and to remain in existence in association with the derived matter in any manifestation or phenomenon in different phases is the property of the fundamental dimension energy. In energy matter universe in their phenomenal finite existence in any phase, energy must remain in association with matter. The matter manifests itself in association with energy creating different phases. The change of intensities of energy and matter and the changes of their intensities from phase to phase in sequence have been explained in fig. 2. In an exactly identical manner the numerical continuum of fundamental unit and the digits in combination have been explained in figs. 3 and 4. The ultimate fundamental is one unit. The digits vary from 1 to 9. The unit and the digits in combination make the different inertial frames of phases of numbers from 1 to 10, 10 to 100, 100 to 1000 and so on. The nature of association will be obvious from the figures. The critical states correspond to the thermodynamic critical states of two, in which the first critical state of one in which the unit is in combination with nil magnitude of digit and in the 10th state the magnitude of digit is 9 which in combination with the fundamental unit makes it 10 for this second critical state, which would be fundamental for the subsequent phase of 10th in which at the critical state of 10, which is the second critical state, at which state the magnitude of subsequent digits in association with 10 is zero, whereas at the 3rd critical state of 100 the magnitude of derived increases to 90 in combination with fundamental 10 and the combined total of 100 for the subsequent phase, 100 becomes the funda-

mental for the 100th phase. The digits in association increase from zero at the third critical state through 100, 200, . . . towards 900 at the 4th critical state of 1000. The continuum in this way progressively proceeds. The variation of intensity of the digits and unit as derived and fundamental respectively in their combined magnitude of numbers in the continuum has been explained in fig. 5 in which at the first critical state of 1, the magnitude of digit in association with it was zero or nil. The intensity of the fundamental unit is thus 1/1 whereas the intensity of digit is 0/1. The state is one of all fundamental as unit. As the magnitude of number increases the intensity of unit decreases. Thus from the first critical state intensity of one as 1 decreases to 1/10 at the second critical state of 10, whereas the intensity of digits starting with nil at the first critical state of 1 as 0/1 progressively increases in the first inertial frame in combination with fundamental unit to 9/10 which is maximum at second critical state. From the critical state of 10 in the inertial frame of 10th, the fundamental is 10 starting with the intensity of $10/10=1$ at critical state of 10, progressively decreases to $10/100$ at the 3rd critical state of 100 and the intensity of the derived digit starting with least as 0/10 at second critical state progressively increases to maximum as $90/100$ at the third critical state of 100 and so on.

Critical States

From these figures one very significant and important aspect in the definition of critical state which can be discerned is that, it is a constant state, at which the change takes place from one phase to another. The transition at this equality equilibrium state occurs from the least and highest intensities of fundamental and derived respectively of the previous phase to maximum and minimum intensities of fundamental and derived of the next phase. The variation of combined magnitudes of the numbers through the various critical states and corresponding inertial frames as shown in fig. 4 and the variation of intensities of 1 and the digits in their combined existence in the continuum of numbers at the

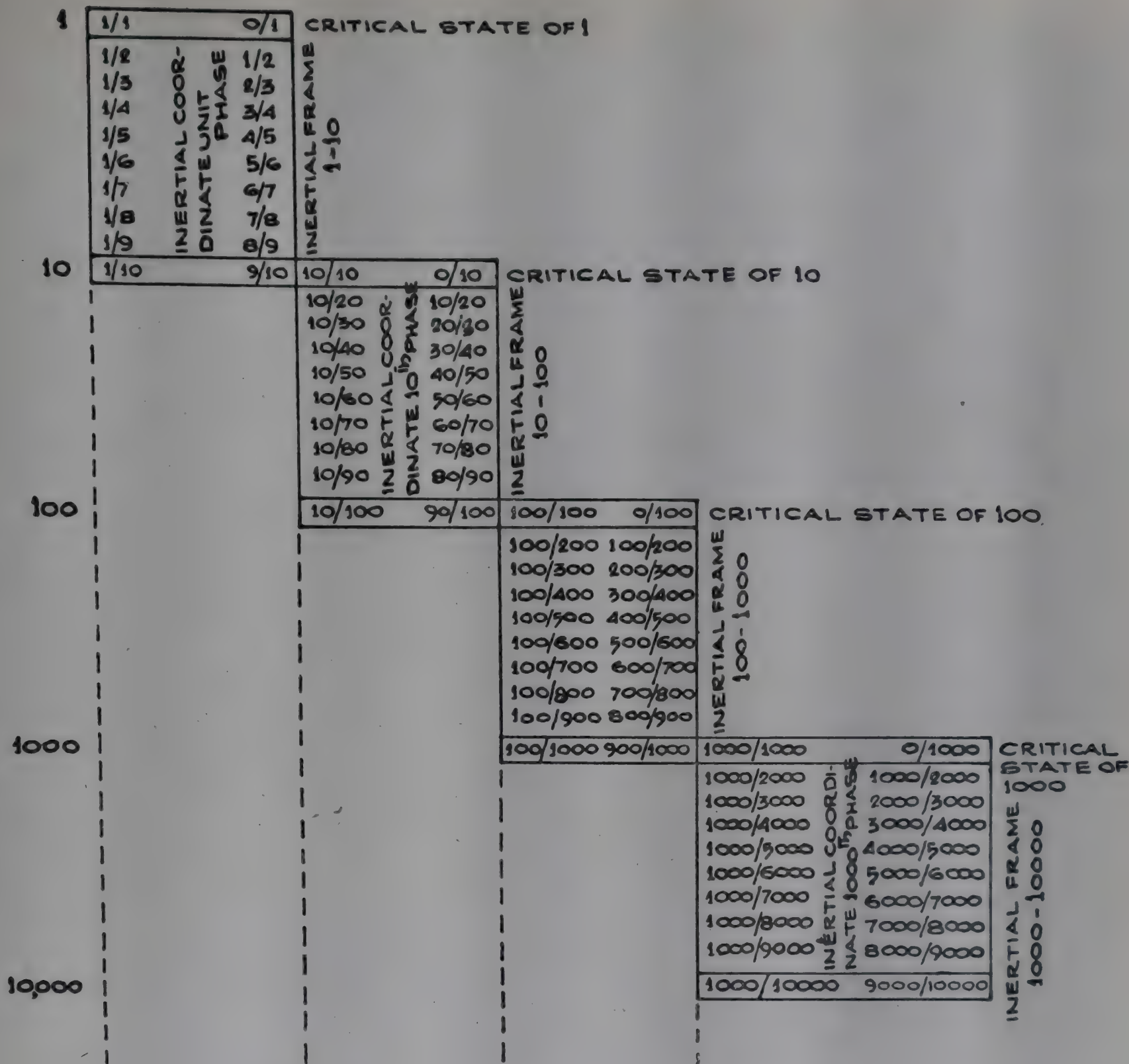


Fig. 5—Continuous Variation of Intensities of One and Digits in the Continuum of Numbers

various critical states and phases as shown in fig. 5 demonstrate the nature of the continuum clearly.

Concept of Fundamental Unit of Absolute One

Let us examine the concept of one absolute unassociated with anything in the first critical abstract state and its transition from that state through the finite phenomenal manifestation of numbers in combination with digits in one inertial reference frame of co-ordinate in which the first fundamental 1 progressively decreases

in intensity in combination with the digits of increasing intensity. As the magnitudes of numbers increase towards the next critical state of 10, the intensities of 1 progressively decrease from 1/1 to 1/10 while the intensities of digits increases from 0/1 to 9/10. At the critical state of 10 transition from previous to new phase occurs generating a new fundamental for that phase and the derived digits for that new phase.

These essential aspects and the concepts behind these were at the root and were the origin of the philosophical

postulates of the ancient, viz. in the Sankhyya, Naya, Vaisheshik and Vedantas as well as in the concept of ultimate God. All these philosophies are identical with the concept of absolute one and its transition from its absolute concept to finite phenomenal and the transition from previous phase to next phase; each phase having a fundamental for it as well as a derived in combination leading to the concept of God's status in terms of expressions like Brahman, Atman, Indriya, Tanmatra or Agni, Vayu, Brahma, Vishnu, Shiva and so on and so forth. The realisation of the transition of the properties of the ultimate fundamental and derived in combination manifesting the phenomenal phases in succession was clearly understood in the past, as would be seen in the details of the six different Darashanas. In these the first concept starts with the manifestation of the material world as from Vyom through Tej, Marut, Ap towards the most degraded phase as Kshiti. Obviously the change of their properties in terms of their intensities in any inertial frame of single phase and transition from one phase to next through a critical was quantitatively understood and known. Otherwise the evolution of the continuum of numbers and the generation in combination of the various phases in succession as unit, 10, 100, 1000... and the way the fundamental and the derived as digit in combination varying along with their respective intensities and the nature of change which really takes place through the critical states from previous to subsequent could not have been possible. This mechanism of evolution of numbers in continuum of such phases as the continuum of phases from space towards gas, liquid, solid, are absolutely identical and could not have been perfected unless knowledge existed about the phases and the changes of their properties, particularly the significance of intensities or densities, while changes take place from one to next in sequence with reference co-ordinate as yardstick of temperature as Tapas.

(2) Decimal Continuum

In the continuum of numbers it may be noted that the first magnitude in the finite combination of the numbers is 2 which is one of fundamental and one of derived digit. In fig. 4 we have elaborated the inertial reference co-ordinates of 10th phase from 10 to 100 and now has been further elaborated showing the transition through various phases as 10th, 20th, 30th, 40th and so on. One of the most important issue which arose is to know the exact nature of mechanism involved towards approaching the absolute 1 in the number from the finite combined magnitude of 2. The ultimate state is a fundamental unit in which the intensity of funda-

mental absolute is 1/1 whereas in the finite combination of 2 the intensity of fundamental is 1/2. The question is—how the intensity of one (1) would increase from 1/2 to 1. On the other side the transition of the magnitude of digit as 1 occurs towards 0 at the critical state of fundamental one—how does it occur? What is the mechanism through which this would proceed?

This mechanism has been illustrated in figs. 6, 7 and 8. In fig. 6 the combination of fundamental unit with the digits making the continuation of magnitude of numbers has been presented. The magnitude of 1 is shown in axis AA and along the axis BB the digits have been shown which is in combination with fundamental. In fig. 8 the combined total as magnitude of numbers is shown. In fig. 7 the variation of the digits only has been shown in the continuum from the highest towards least.

It may be seen from fig. 6 that the change of the combined magnitude of the fundamental unit and the digit starting from the combination 1+1 towards absolute 1 in which the magnitude of the digit in combination would be nil, proceeds through various phases of 10th, 100th, 1000th as against transition of the magnitude through various phases for reciprocals as against unit 10, 100... increasing order of magnitude. The nature of opposite changes from the combination of 1+1 towards increasing order of magnitude of fundamental and decreasing order of magnitude of derived is obvious. In the direction of decreasing order of magnitude of digit 1 from the combination 1+1, the fundamental unit progressively increases in magnitude through various phases as 10/9 to 10/11 in one inertial frame in which the intensities of the digits vary as 9/19 to 1/11. In the 100th phase the intensity of fundamental varies as 100/109 to 100/101. The intensity of digit varies from 9/109 to 1/101. In the next phase the fundamental increases in intensity from 1000/1009 to 1000/1001 and the digit varies from 9/1009 to 1/1009 and so on, till the magnitude of intensities of the digits in association with fundamental unit progressively decreases in combination from .9 through .09, .009 till at the state of absolute 1 the number of zeros after the decimal point is infinity. At that state the nature of magnitudes in combination with the fundamental unit and corresponding digit would be 1 and .0000 to infinity respectively, in which state the intensity of one is 1/1 and the intensity of the magnitude of digit is: $\frac{.000 \text{ to infinity}}{1}$ which is nil.

(3) Concept of Zero, One and Infinity

Consider the critical state of absolute one. This should

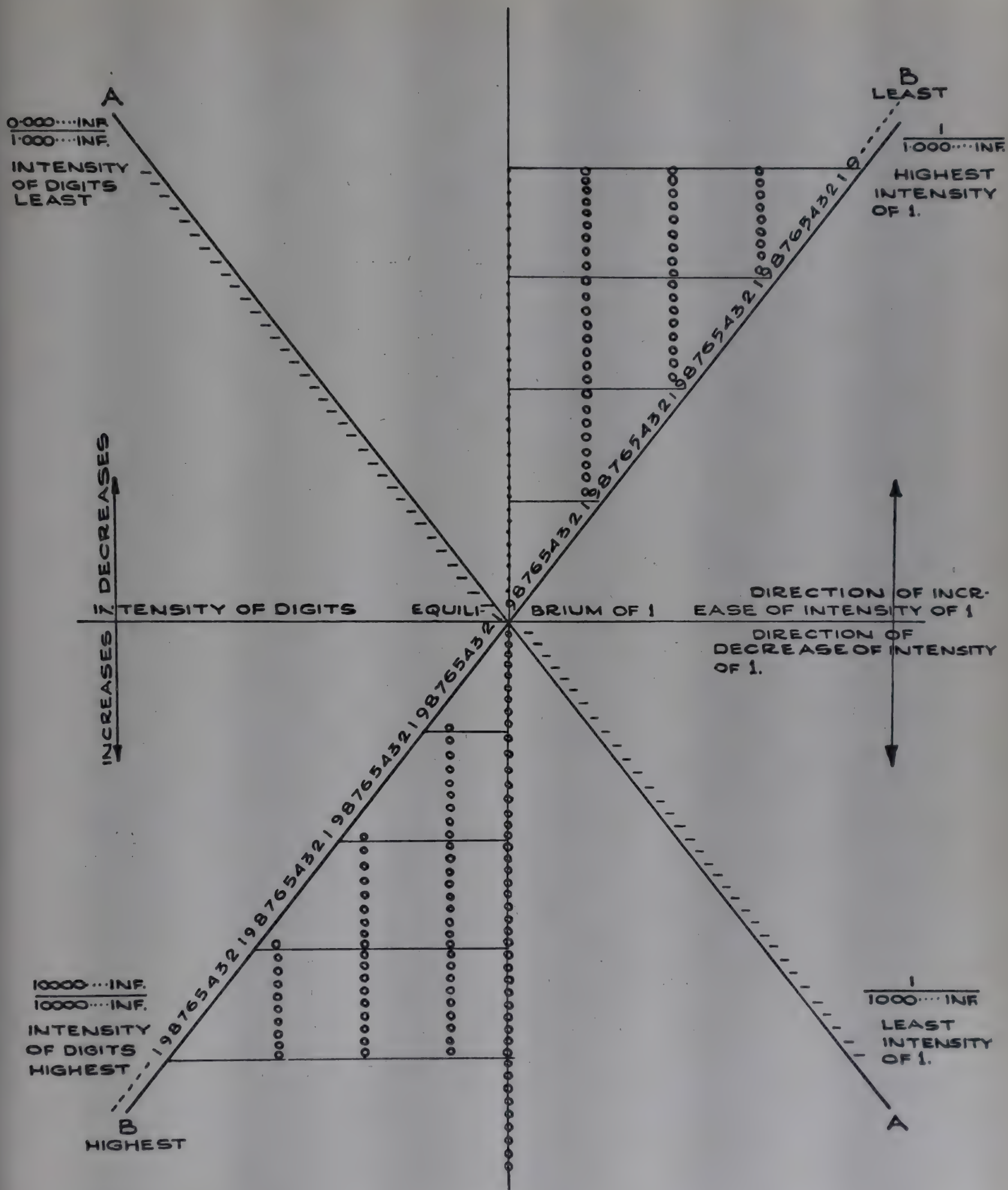


Fig. 6

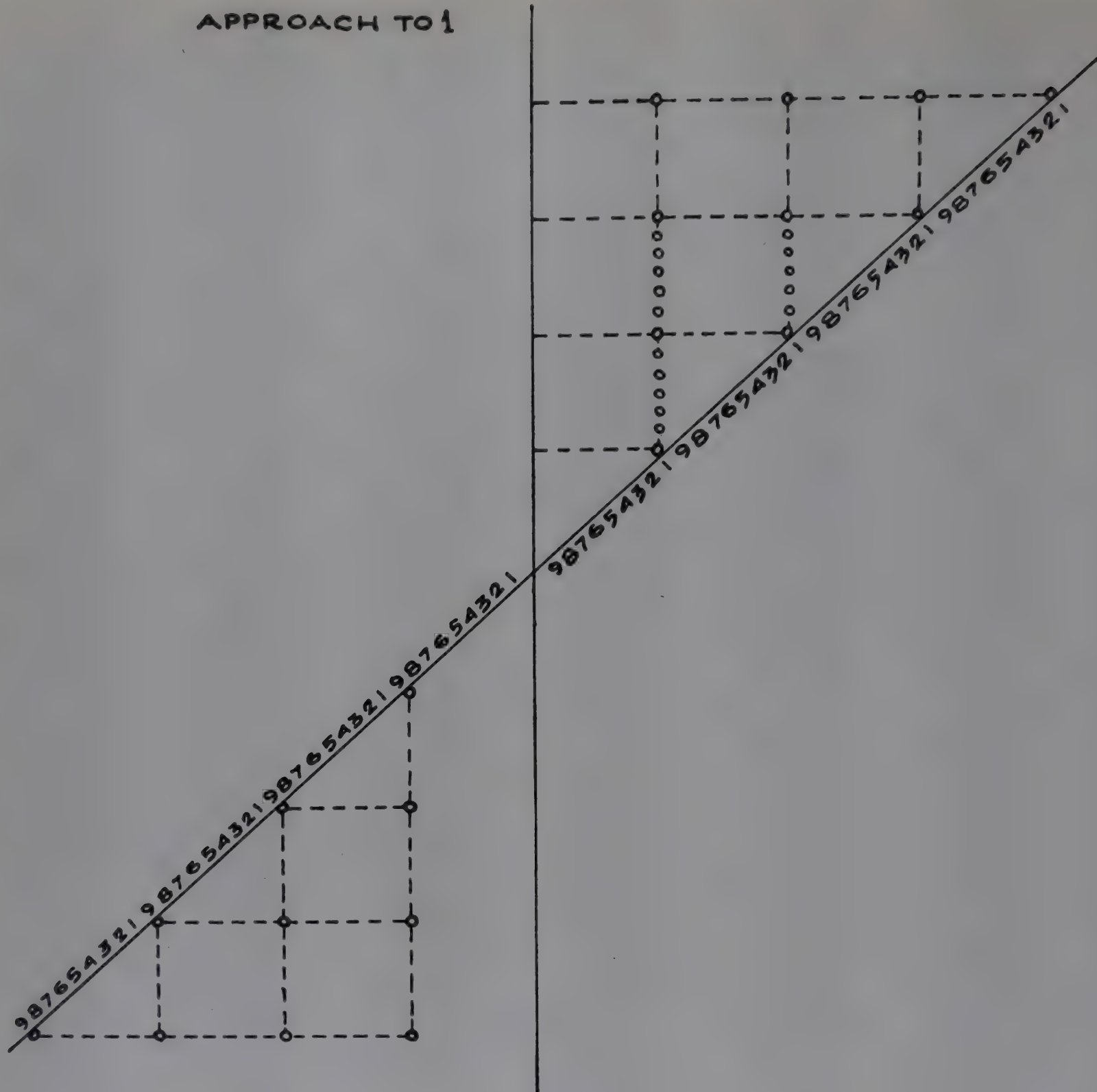


Fig. 7

be obvious from the figures and the subsequent deductions therefrom as explained before. At that state the magnitude of associated digit is nil or absolute zero, which is symbolically presented as .000000....inf. and the magnitude of number one is 1.000000....inf.

Sum total of the intensities

$$\frac{1 + .000 \dots \text{inf.}}{1.000 \dots \text{inf.}} = 1 \text{ [Since } \frac{1 + .00 \dots \text{inf.}}{1 + .00 \dots \text{inf.}} = 1.]$$

And the individual intensities are

$$\frac{1}{1.000 \dots \text{inf.}} \text{ and } \frac{.000 \dots \text{inf.}}{1.000 \dots \text{inf.}}$$

$$\text{But } \frac{1}{1.000 \dots \text{inf.}} = 1; \text{ which leads to } \frac{.000 \dots \text{inf.}}{1.000 \dots \text{inf.}} = 0$$

$$1 + \frac{.000 \dots \text{inf.}}{1.000 \dots \text{inf.}} = 1 \text{ [unless } \frac{.000 \dots \text{inf.}}{1.000 \dots \text{inf.}} = 0 \text{ —this relation cannot hold good.]}$$

APPROACH TO 1

$1+1=2$
 $1+2=3$
 $1+3=4$
 $1+4=5$
 $1+5=6$
 $1+6=7$
 $1+7=8$
 $1+8=9$
 $1+9=10$
 $10+10=20$
 $10+20=30$
 $10+30=40$
 $10+40=50$
 $10+50=60$
 $10+60=70$
 $10+70=80$
 $10+80=90$
 $10+90=100$
 $100+100=200$
 $100+200=300$
 $100+300=400$
 $100+400=500$
 $100+500=600$
 $100+600=700$
 $100+700=800$
 $100+800=900$
 $100+900=1000$
 $1000+1000=2000$

$1.000...INF$
 $1.0009 = 1 + .0009$
 $1.001 = 1 + .001$
 $1.009 = 1 + .009$
 $1.01 = 1 + .01$
 $1.09 = 1 + .09$
 $1.1 = 1 + .1$
 $1.2 = 1 + .2$
 $1.3 = 1 + .3$
 $1.4 = 1 + .4$
 $1.5 = 1 + .5$
 $1.6 = 1 + .6$
 $1.7 = 1 + .7$
 $1.8 = 1 + .8$
 $1.9 = 1 + .9$

1 ADDED

Fig. 8

As corollary $\frac{.000\dots\text{inf.}}{1.000\dots\text{inf.}} = 1-1=0 \text{ nil.}$

Summarising $1 = \frac{.000\dots\text{inf.}}{.000\dots\text{inf.}} = \frac{1.000\dots\text{inf.}}{1.000\dots\text{inf.}} = \text{one as intensity}$

$0 = \frac{.000\dots\text{inf.}}{1.000\dots\text{inf.}} = \text{nil as intensity}$

Relativity of identicals

indistinguishable $= \frac{1}{0} = \frac{1}{.000\dots\text{inf.}} = \frac{1.000\dots\text{inf.}}{.000\dots\text{inf.}} = \text{infinity as intensity}$

$\frac{0'}{0'} = \frac{.000\dots\text{inf.}}{.000\dots\text{inf.}} = \frac{1}{1} = 1$ If the two zeros are identical this ratio is =1.

The above leads to the conclusion that:

anything identical divided by same =1

anything identical—same identical =0

relativity or ratio of perfect opposites is either α or nil

i.e. $\frac{1}{0}$ or $\frac{0}{1}$

If the two are different then the relativity of two differentials say a/b is either $< \frac{1}{1}$ or $> \frac{1}{1}$.

But the relativity of two identicals whether indistinguishable or distinguishable is always 1.

Thus $\frac{0'}{0'} = 1, \frac{.000\dots\text{inf.}}{.00\dots\text{inf.}} = 1, \frac{1.000\dots\text{inf.}}{1.000\dots\text{inf.}} = 1$

And as a corollary $\frac{.000\dots\text{to say three places}}{.000\dots\text{to say three places}} = 1$

Finally this leads to $\frac{0}{0} = 1$ Provided the two zeros refer to identical position (placement) and status.

Similarly relativity of any two identical magnitudes would also follow same pattern as say $\frac{2}{2}, \frac{3}{3}, \frac{4}{4}$ which are all 1.

Definition of indistinguishableness of only one is indescribable, since it is incomprehensible in human perception. The problem therefore is then how to define that state. It is however possible to analyse a state of distinguishables of identicals in the background of indistinguishable one. The criteria for such distinguishable could be:

Firstly, if they are distinguishable identicals it would be possible to add them to get a sum total. Secondly, it should be possible to distinguish by difference between them; thirdly, it should be possible to multiply them and fourthly there should be a relativity or ratio between

them. These 4 criteria could be represented by the mathematical signs $+, -, \times, \div$. The state of absolute one is a state in which there is only one of fundamental in which derived (as distinguishable) is nil, i.e. the magnitude of digit associated with fundamental one to make the number one as 1 is nil, or say absolute zero. It could be expressed as absolute 1 or 1.000...inf. as has been deduced in the previous section. The criteria of the previous state of absolute 1 from which next higher magnitude of digit bigger than nil will start would depend on the criteria of imaginary digit nil in association with one fundamental (which is also imaginary) in its absolute state. In the absolute state of fundamental one the association of derived nil could have also the following 4 imaginary criteria of derived in association with indistinguishable fundamental:

$0+0, 0-0, 0\times 0, 0\div 0$

These 4 combinations of 0 as nil which was in combination with fundamental absolute one in its indistinguishable state will produce the magnitude of digit 1 as the subsequent, since the sum total of the effects as $0+0, 0-0, 0\times 0, 0\div 0$ is equal to only 1 (since $\frac{0}{0} = 1$).

The above deduction will be in conformity with the following explanation:

Imagine a state in which the distinguishable ones are all identical in an indistinguishable background. The distinguishable identical should be capable of being added, differentiated, multiplied and have relativity. So long as the distinguishables will remain identical, we have seen previously, that their relativity irrespective of their individual magnitudes will be also one which was described previously as $0/0=1, 1/1=1, 2/2=1, 3/3=1$ and so on. If we assign magnitudes to the distinguishable identicals, the criteria of the previous states which will yield the magnitudes of the subsequent states would be illustrated in the following manner:

$0+0=0$	$1+1=2$	$2+2=4$
$0-0=0$	$1-1=0$	$2-2=0$
$0\times 0=0$	$1\times 1=1$	$2\times 2=4$
$\frac{0}{0} = 1$	$\frac{1}{1} = 1$	$\frac{2}{2} = 1$

Sum total is 1 Sum total is 4 Sum total is 9 and so on.

This would show how the increasing magnitudes of derived distinguished identicals will be generated, in the background of one indistinguishable fundamental, in sequence from a previous to a next state in sequence and form the continuum 1, 4, 9, 16... (in terms of square of number of unit squares as $1^2, 2^2, 3^2, 4^2\dots$) which is continuum of squares in increasing order of magnitude in one direction.

CHAPTER 3

Four Dimensional Tetrahedral Evolution Represented as Continuum of Squares in a Plane : Criteria for Development of Square Continuum and Numerical Continuum

(1) Evolution of Continuum of Squares in a Plane

We shall now explain the transition from an indistinguishable phase to distinguishable identicals and distinguishable differentials. The concept of the phase of indistinguishableness of identicals, through the concept of continuum of squares in a plane of distinguishable identicals and distinguishable differentials may be realised from the concept of plane surface as indistinguishable, which subsequently can be rendered distinguishable by a continuum of identical units of squares. The plane surface before any configuration is imprinted in it, is one concept in which there is nothing which can be distinguished from one position or other. As soon as a square in it is imprinted the configuration gives in the background of indistinguishableness of plane surface towards a concrete or objective definition in the form of square and square units on plane surface. The subsequent development of continuum of squares follows the sequence as 1, 4, 9, 16. This is illustrated in fig. 9.

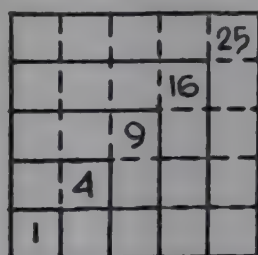


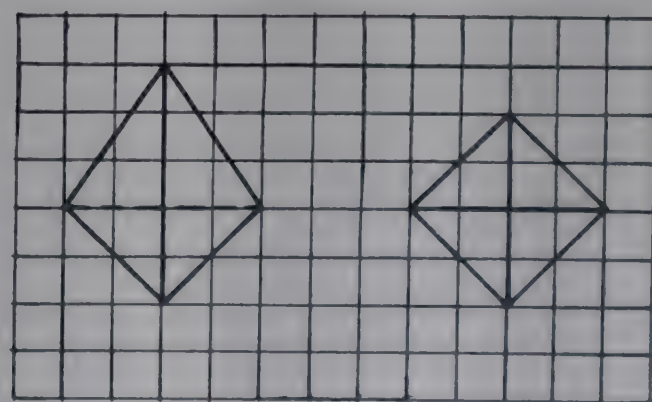
Fig. 9

The similarity of this evolution of magnitudes as squares in a continuum in a plane surface is similar to the evolution of numbers from the state of indistinguishable absolute 1, in association with nil magnitude of digit as 0, in increasing magnitudes of digits as 0, 1, 2, 3, 4.. which has been explained before.

It is however, necessary to explain the special significance of the concept of plane surface continuum of identical units of squares in the background of plane surface. We have to explain the relationship of the square continuum in a plane vis-a-vis the 4 dimensional space time continuum of the manifested universe. The theory of universal wave and the new theory of unified field continuum show that the isotropic configuration from a state of point of position of indistinguishableness would

be generated from two opposite dimensions like fundamental and derived. Fundamental having the property of emanation from imaginary point of position and the derived having the property of converging of the emanated ones towards a perceivable point of position. The configuration of evolution must assume the configuration of regular tetrahedron in which with respect to the centre of the tetrahedron, the four evolved positions are isotropic and with respect to any evolved position of the tetrahedron the other three also are isotropic. But it is difficult to express evolution in 4 directional co-ordinates. If one would want to describe the evolution, other than in the 4 directional manner, so that the configuration is more amenable to perception and comparatively easy to understand then some other mode of presentation is required. One mode of presentation could be to transfer the 4 directional concept to a plane surface square continuum. While doing so and analysing the projected manifestation from 4 directional manifestation to a plane surface configuration one must also remember the limitations that are involved between the relative configurations of plane surface square continuum vis-a-vis the original and actual 4 directional tetrahedral configurational manifestation.

The regular tetrahedron when placed on one edge parallel to a plane surface with the centre, coming directly above the edge, the projected configuration of the tetrahedron on plane surface assumes the configuration of square as shown in fig. 10.



Triangular
Tetrahedron

Square on
Plane Surface

Fig. 10

In this projected figure as square the magnitudes of the various dimensions of the original tetrahedron undergo changes in their magnitudes in the projected square. For example the diagonal of this square retains the same magnitude of $2\sqrt{2}\sqrt{3}$ of the side edge of the tetrahedron. But the other 4 sides of the original tetrahedron become the 4 sides of the projected square on plane surface. The magnitude of the side of the square on plane surface is not $2\sqrt{2}\sqrt{3}$, but is $2\sqrt{3}$. The magnitude of unit distance in this evaluation being 1, which is the distance between the centre of the tetrahedron to centre of any of the triangular faces.

Further, in the 4 directional tetrahedral scheme the evolution from central tetrahedron to the progressive phases by addition of tetrahedron with the intervening spaces, however, would not be apparently realised from the projected configuration in the plane surface in the square continuum of plane surface. In order to depict that configuration by square continuum on plane surface in proper perspective, then, what would happen in 4 directional configuration was realised in ancient times and has been illustrated elsewhere*.

Perception of universal space time phenomena in reality, involves 4 directional co-ordinates, if that would be attempted to be derived from data or relationship obtained from projected plane square continuum, then those must therefore have to be modified and transformed also in proper perspective. It is thus clear that when one would attempt to analyse any 4 directional phenomena by translating the picture as projected on a plane surface, and with the help of laws that govern the relationship of configurations on plane surface only, to interpret results which would be applicable to 4 direction phenomena, these relationships must be modified and transformed to suit their applicability in the 4 directional evolutionary continuum. The concept of continuum of unit squares in a plane from the background of indistinguishableness towards distinguishable identical units of squares and the mechanism of how from a previous state the magnitudes in subsequent states are generated in square continuum have been indicated in the above as $1^2, 2^2, 3^2, 4^2, \dots$. If at a plane this would be considered in all 4 directions (as explained in the above) the increasing magnitude of squares forming the continuum would be $4 \times (1^2, 2^2, 3^2, \dots)$. It may be noticed that in the continuum the magnitudes as 1, 2, 3, 4, ... are in increasing

order but are in terms of their own squares. These are not co-efficients indicating numbers of unit squares.

If, however, the continuum would be expressed in the plane as increasing magnitudes of squares of increasing numbers of unit squares (in terms of co-efficients of unit squares) as explained in fig. 12 the evolutionary picture will be entirely different. In order to find out the nature of evolution of increasing magnitude of co-efficients of unit squares it will require to know the concept of the square (definition of the square). The square is a configuration on a plane in 2 directional continuum projected from the concept of 4 directional regular tetrahedron. Tetrahedron is a conception and the projected square on a plane surface is perception. The inter-relationship between the various dimensions of squares in a plane is of one kind. Those relationships when translated to regular tetrahedral configuration would be different. For example in the square configuration projected on a plane, square on the diagonal which was one of the sides of the regular tetrahedron is not the same as the square on the side of the projected square, which was also a side of the regular tetrahedron, because of its different magnitude it assumes when projected on the plane surface.

(2) Relationship of Squares on Diagonal of Unit Square with the Square on the Sides

The continuum of identical unit squares in a plane has been shown in fig. 11. In this both the sides of the

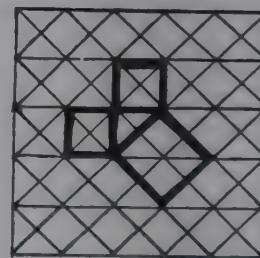


Fig. 11

squares as well as the diagonals also are simultaneously printed. In this continuum, it may be noticed, there are 3 types of configurations. The unit squares of identical in nature and square units on the diagonals of unit squares and thirdly, the continuum consist of identical units of right angled isosceles triangles.

The quantitative relationship between the three configurations would be obvious from a look at the fig. 11. It may be seen that the square on the diagonal of unit square contains 8 numbers of identical right angled

* Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol.* 5 (2A) (1968), 55 (figs. 27-30)

isosceles triangles, whereas each unit square contains only 4 such triangles. It is obvious that the square on the diagonal is equal in magnitude to 2 unit squares. If the relationship between the sides and hypotenuse of the right angled isosceles triangle is expressed quantitatively then it would be as follows:

Square on the hypotenuse = sum of the squares on the two equal sides

Every one knows the far reaching importance of this deduction. The discovery, however, of this from a configuration of continuum of identical unit squares with their diagonals can be deduced from very elementary analysis and common sense perception of this relationship from a glance at the figures. This elementary deduction does not require any knowledge of sophisticated geometrical or mathematical theories. But only common sense analysis and perception enables this deduction. In the ancient times when this elementary observation, of fundamental importance, was discovered, that did not require any background knowledge of sophisticated scientific or mathematical theory, but mere common sense. But the observation became the original basis of development of mathematics, geometry and laid the foundation of future science.

After realisation of the relationship between squares on the two equal sides and that on hypotenuse of right angled isosceles triangle, obviously inquisitiveness, enquiry and research were continued to find out relationship between the square on hypotenuse and the sum of the squares on other sides of any right angled triangle having unequal sides.

Reverting to fig. 11, if the magnitude of the sides of the unit square is 1, the magnitude of diagonal of unit square which is same as hypotenuse of the unit right angled triangle is $1\sqrt{2}$. If the same relationship would be expressed in terms of co-efficients of square unit then the square unit would be expressed as 1.1^2 and the square on the hypotenuse would be expressed as 2.1^2 . If, therefore, one would like to get a picture of the continuum in which the magnitude of squares would be in terms of 1 sq. unit, 2 sq. units, 3 sq. units . . . then for the generation of configuration of continuum of such squares would require the knowledge of relationship of squares on the hypotenuse and sides of right angled triangle of one unit magnitude.

The minimum magnitude to start with is equal to the side of a unit square. The diagonal of this unit is the hypotenuse of the right angled isosceles triangle, square on which is equal to 2 square units. If with this hypotenuse of two unit square magnitudes any right angled

triangle is formed by adding one side of unit square at right angle, then square on the new hypotenuse will be equal to 2 square units + 1 square unit = 3 square units. If to this new hypotenuse another side of unit square is added at right angles to it, it will generate similarly another right angled triangle, the square on that hypotenuse will be equal to 3 square units + 1 square unit = 4 square units and so on. This has been illustrated in fig. 12. In fig. 12 'a' is a side of the unit square and has magnitude of 1 unit of length. The magnitude of diagonal of the unit square on b has magnitude of 2 unit squares. The sides a, a, a, a, are all of magnitude 1 and are one side of unit square.

It may be seen from fig. 12 that the magnitude of the hypotenuse of the right angled triangle starting with right angled isosceles in the unit state when it is increased, the magnitude of the square on the hypotenuse increases by 1 unit square. Out of the 2 angles of the right angled triangle one progressively decreases at the centre of the spiral and the other angle on the periphery increases with increase of magnitude of hypotenuse. It can be visualised that at infinite length of hypotenuse the angle of the right angled triangle at the centre would tend to reduce to zero and the other angle at the periphery would tend to be a right angle, At that state the ratio of hypotenuse to the side of unit square would tend to infinity, and the 2 hypotenuses, one previous and the next, would tend to coincide to form the radius of infinite magnitude of circle.

However, so long as the concept of right angle will remain, the formation of circles in this mode of increase of magnitude of hypotenuse will never come to that state.

Fig. 12 gives the nature of the continuum of increasing magnitudes of squares on hypotenuses in terms of number of square units as 1, 2, 3, 4....Further fig. 12 also gives the picture of continuum of increasing linear magnitudes as diagonal of square and rectangles of increasing magnitudes of area. These increasing linear magnitudes are $1\sqrt{1}$, $1\sqrt{2}$, $1\sqrt{3}$, $1\sqrt{4}$, $1\sqrt{5}$

The significance of these increasing magnitudes as $\sqrt{1}$, $\sqrt{2}$, $\sqrt{3}$... in the continuum of increasing magnitudes of dimensions of co-ordinates in terms of powers will be explained later.

(3) Two Modes of Magnitudes in Square Continuum in a Plane

There could thus be two modes in which the increase of magnitude of squares could progressively develop in plane surface continuum in one direction. The first mode

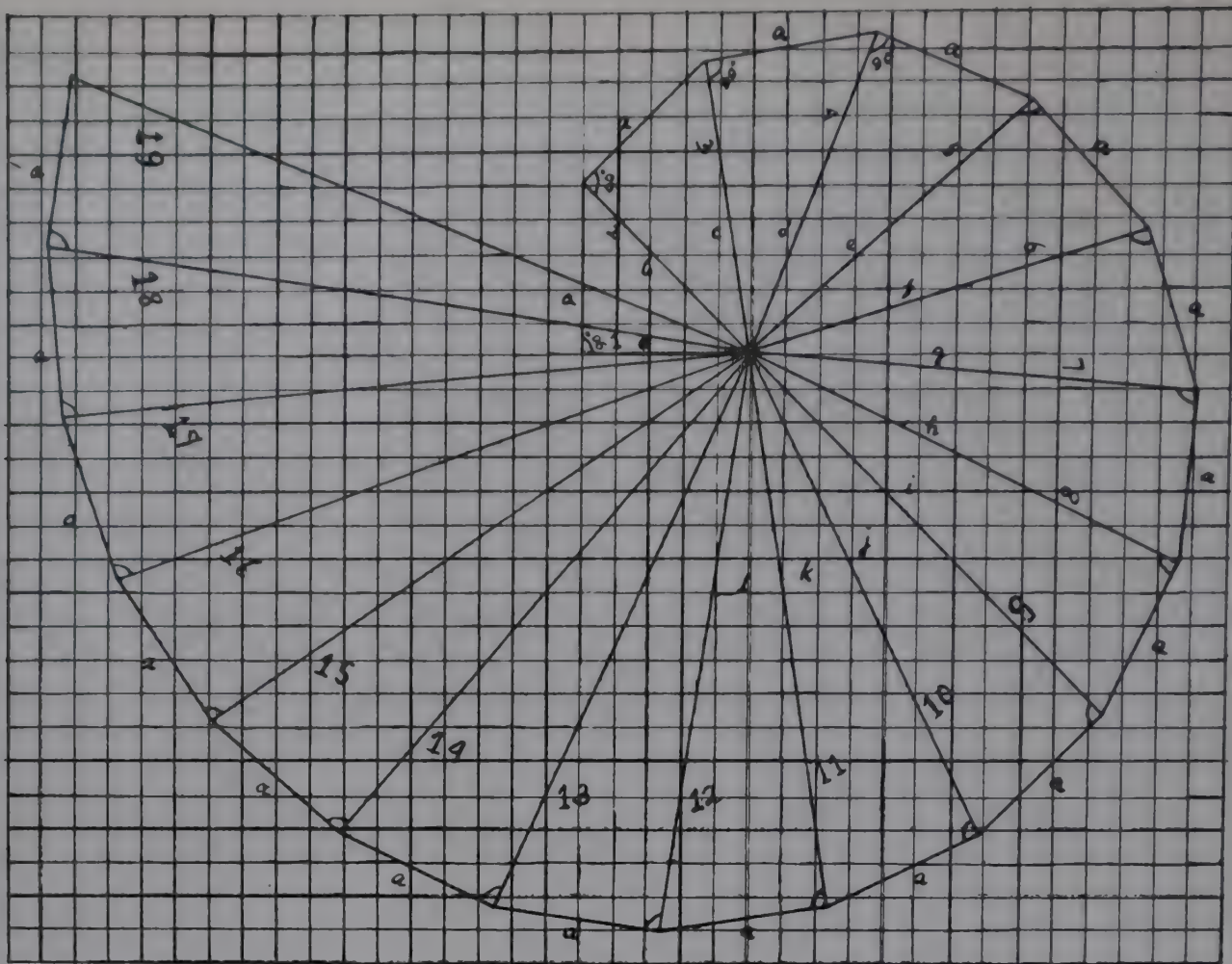


Fig. 12—Increasing Magnitudes in Terms of Number of Square Units

would be as shown in figs. 9 and 11 which follows $1^2, 2^2, 3^2, 4^2, \dots$. The second mode would be as shown in fig. 12 in which the increasing magnitude of the squares would follow the pattern: 1 sq. unit, 2 sq. units, 3 sq. units....

Obviously the laws governing the progressive increase of the magnitudes of squares in the two cases are different. Suppose that the first square is one unit square, then in both cases it is of same magnitude. In the first mode starting with 1^2 the next higher magnitudes of squares are $2^2, 3^2, 4^2, 5^2, \dots$ which means that 4 unit squares can assemble to make full square, similarly in the next state 9 square units make a perfect square and so on. In the second mode, however, the first magnitude of square is one unit square and the magnitude of the second square is equivalent to sum of 2 square units and the magnitude of the subsequent squares in the series would be equal to sum of 3 unit squares, 4 unit squares and so on.

The development of increasing magnitudes of squares in the second mode involves the relationship between the magnitude of square on the hypotenuse and the sum of the squares on the sides of right angled triangle. The significance of two kinds of magnitudes of squares in plane continuum has far reaching consequence in our

conventional concepts of magnitudes in phenomenal existence. One kind of magnitude in square continuum is as $1 \times 1^2, 1 \times 2^2, 1 \times 3^2, 1 \times 4^2, \dots$ and the other kind is expressed as $1 \times \sqrt{1}, 1 \times \sqrt{2}, 1 \times \sqrt{3}, \dots$. The first kind of magnitudes are themselves squares and second kind are their roots; variation in the first case is in two dimensional co-ordinate and the variation in the second case is unidimensional or linear co-ordinate. When we talk of magnitude and its variation, we must therefore first ensure in what co-ordinate systems the magnitude is reflected and intended to vary making a continuum. Is it within a constant co-ordinate system or its variation involves different co-ordinate system? This aspect will be further discussed in a later section on discussion on magnitude.

The development of increasing magnitudes of squares in the continuum in the first mode is elaborated in the following.

(4) Criteria for Developments of Squares in a Plane

It has been explained before that the evolution occurs in phases in succession in the direction of (decreasing) intensity gradient of the fundamental i.e. cause. The effect in combination with cause at first increases in intensity to maximum towards a critical

state, after which change of phase occurs and from which the effect progressively decreases in intensity in continuity and a new phase starting with minimum increases to maximum at next critical. In evolution cause and effect in succession must be involved. Appearance of a subsequent phase cannot but be from a previous phase. At any critical state from which a new phase develops the perceivable knowledge about the previous phase by the new phase is impossible. The critical indistinguishable state with respect to the new phase is the first state from which the new phase develops and progresses increasing in magnitudes. In the evolution of magnitude of squares in plane surface continuum it starts with a unit square from a previous background of indistinguishableness of plane surface having no configuration. The next phase is the distinguishable identical of unit squares in a continuum in which all the unit squares are identical, but they are distinguishables in the background of indistinguishable plane surface. These are shown as follows:

In the indistinguishable phase the distinguishables are of nil magnitudes in association; therefore criteria of development of identical distinguishables are:

- (a) $0+0=0$ Here 0 is distinguishable identicals
 $0-0=0$ of nil magnitude in the background
 $0 \times 0=0$ of all of one indistinguishable
 $0 \div 0=1$ whole.

When distinguishable identicals as cognisable magnitudes as digits appear in the background of indistinguishableness of one, the criteria of association would be:

- (b) $1+1=2$ $2+2=4$ $3+3=6$
 $1-1=0$ $2-2=0$ $3-3=0$
 $1 \times 1=1$ $2 \times 2=4$ $3 \times 3=9$ A
 $1 \div 1=1$ $2 \div 2=1$ $3 \div 3=1$
Sum total 4 Sum total 9 Sum total 16

Here increasing magnitudes of the squares in terms of the numbers of identical square units in the continuum are as 1, 4, 9, 16... and in terms of squares of numbers of unit squares as $1^2, 2^2, 3^2, 4^2, \dots$

In the continuum, when squares of distinguishable different magnitudes would be formed, the criteria for formation of squares of increasing magnitude in subsequent states can be illustrated by the following examples:

Distinguishable different

- (c) $1+1$ $1+2$ $1+3$
 $1-1$ $1-2$ $1-3$
 1×1 1×2 1×3
 $1 \div 1$ $1 \div 2$ $1 \div 3$ B

					Sum total	
(d)	$1+1$	$2+1$	$3+1$	$4+1$	$4(1, 2, 3, 4, \dots)$ $=2^2 (1^2/1, 2^2/2, 3^2/3, 4^2/4)$ C	
	$1-1$	$2-1$	$3-1$	$4-1$		
	1×1	2×1	3×1	4×1		
	$1 \div 1$	$2 \div 1$	$3 \div 1$	$4 \div 1$		

					Sum total	
(e)	$1+2$	$2+3$	$3+4$		$\frac{1}{2} 3^2, \frac{2}{3} 4^2, \frac{1}{4} 5^2$	D
	$1-2$	$2-3$	$3-4$			
	1×2	2×3	3×4			
	$1 \div 2$	$2 \div 3$	$3 \div 4$			

					Sum total	
(f)	$2+1$	$3+2$	$4+3$		$\frac{2}{1} 2^2, \frac{3}{2} 3^2, \frac{4}{3} 4^2$	E
	$2-1$	$3-2$	$4-3$			
	2×1	3×2	4×3			
	$2 \div 1$	$3 \div 2$	$4 \div 3$			

Sum total
General formulae
 $\frac{X}{Y} (Y^2+2Y+1)$ or
 $\frac{X}{Y} (Y+1)^2$

It may be noted that in the four alternative criteria illustrated, the relativity of the differentials in all the alternatives c, d, e and f are not identical. They all are differentials in each case in all the alternatives. The resultant magnitudes of the squares are determined by the product of the relativity with the expected square magnitudes.

There is, however, one law which has been deduced from the alternatives, which governs the development of the progressive magnitudes in succession from previous to next, which can be presented by the formula viz.,

$$X/Y(Y^2+2Y+1)$$

in which X and Y are the relative magnitudes of the two different magnitudes of squares. By inserting numerical values, any subsequent magnitude of squares from the previous state to next can be found out in all the alternatives, in the case of distinguishable identicals as well as the distinguishable differentials. For example, take an indistinguishable state in which no distinguishable is present. The magnitude of intensity of distinguishable in the state is nil or 0. These are also identicals. There is no reason why the magnitudes of nils should be different. Thus X and Y are both identical and is 0, then

$$\frac{0}{0}=1 \text{ and } Y^2=0, 2Y=0.$$

Therefore, $X/Y(Y^2+2Y+1)=1 \times 1$ which is equal to 1. Similarly taking the magnitudes of squares in the case of distinguishable identicals the values would correspond to 4, 9, 16, ...

In the cases of distinguishable differentials as indicated in b in association in any of the cases in b, c, d. etc. by substituting their magnitudes for X and Y the resultant magnitude of number of unit squares can be found.

(5) Indistinguishableness, Distinguishableness and Identity in Modern Statistics and in Ancient Philosophies

In modern statistics also the aspects of indistinguishability, distinguishability and distinguishable identity are involved. But indistinguishability in the quantum statistics arises from the uncertainty principle according to which it is not possible to exactly predict the course of a particle and one cannot be identified from the other by any means. The concept of indistinguishability in the present context is; if in concept there would be only one thing or one phase in which no second is associated such a concept of oneness is indistinguishable, a state which however is beyond human perception. This state, which has been the eternal question of indistinguishableness of one, which is associated with no second must be recognised once and for all. The concept of indistinguishableness of a state is same whether in that state nothing exists i.e. a state of nothingness or a state in which all of one exists. Concept of distinct identicals must follow from previous background of indistinguishableness. If BE statistics applies to photons which are identicals but are distinguishables, then a prior background state of indistinguishable photon must exist. Photon is energy radiation. If the phase of distinguishable identical photons is energy, then the prior state in which this phase would merge at higher energy intensity of space must be indistinguishable photonic phase of energy.

In the background of indistinguishable energy when distinguishable identicals or differentials are to be considered the relative variation of intensities of both energy and matter significance must be taken into account. At one energy intensity state identicals of one is possible, but the same one would have different intensities at other energy intensity states. In other words, two particles which are identical cannot belong to two energy intensity states. They must have the intensities or densities corresponding to the energy intensity associated with them. Similarly two identicals when belonging to one energy intensity state cannot have different intensities. They must remain identical. In the basic assumptions of the modern statistics these anomalies remain.

As against the basic concepts in modern statistics, reference would be relevant to the ancient postulates of Sankhya and Vaisheshik Darshanas (in fact all the six

Darshanas). In these the criteria for sq. evolution in a plane surface are $+$, $-$, $\times$ and $\div$, whereas criteria in quantum statistics are three—MB, BE and FD. The major part of the Vaisheshik Darshana concentrates in clarifying these concepts of relative significance of indistinguishableness, distinguishable and distinguishable identicals in association.

Sankhya, Vaisheshik and Nyaya Darshanas concentrate in dealing with and clarifying the various basic concepts which are extremely subtle in nature, but those are involved in building the foundation of the postulates and laws of fundamental science of nature. The concepts of super intensified phase, depleted phase, unsaturated phase, condensed phase, as well as the state of critical equilibrium have been described in great details in the various slokas in Sankhya, Vaisheshik and Nyaya Darshanas. For example in a state of continuum comprising of identical indistinguishable forming equilibrium state, in which the concept of generation of super intensified must be accompanied with simultaneous generation of depleted but indistinguishable phase. But in a state of distinguishable identical units, formation of distinguishable condensed phase, can be realised (perceived) from the simultaneous appearance of generation of depleted phase. The Sanskrit words Atindriya (अतीन्द्रिय), Anumana (अनुमान), Samanya (सामान्य) in the three Darshanas are identical in significance of properties of phases that are associated with critical state (vide Sankhya Karika, Sloka No. VI).

In the Sloka "Traigunam" these are three properties associated with a critical state—properties of phases above critical, below critical and at the critical. These can refer to many aspects, such as intensity termed as Laghu, Sama and Guru—the nature of phases namely one superheated above critical as Abhedha or indistinguishable at critical and below critical as two Bhedas or distinguishables meaning the same as homogeneous and heterogeneous and so on.

Then for conveying the concept of indistinguishableness and distinguishableness of identicals as well as non-identicals have been explained by various illustrative examples in Vaisheshik Darshana by using terminology as Samanya (सामान्य), Vishesha (विशेष), and Avishesha (अविशेष) and so on. In order to distinguish between the state of equilibrium between $(+)$ and $(-)$, positive and negative aspects, numerous arguments have been put forward to explain the concept, particularly in regard to the state of equilibrium at which the positive aspect and negative aspect vanish into an equilibrium neutral aspect, which in terms of positive and negative distincts cannot be explained because they are merged into one.

Then again about the existence of critical equilibrium states having different status or levels depending on the relative intensities of the two opposite aspects between which the critical equilibrium state is established—this has also been explained in great details in these Darshanas. To explain the various concepts, however, illustrative examples have been cited which were available and relevant as well as amenable to understanding in those ancient times when these Darshanas were propounded. For example, to explain the continuum of phases in sequential development (which are the same as the thermodynamic phases in modern science) like solid, liquid, gas, space, and nothing etc., the corresponding words used were Kshiti (Solid), Aap (liquid), Marut (gas), Tej (Space), Vyom (nothing). These, however, in subsequent times, were mis-interpreted to mean earth, water, fire etc. which completely distorted the original objective significance of description of continuum of phenomenal inanimate continuum of phases.

Then again to apply the nature of different continuum and the changes that are involved through the critical states from one phase to next in the continuum in animate domain, the conceivable properties by which human senses can perceive the manifestations, such properties were adopted as Rupa (रूप), Rasa (रस), Gandha (गन्ध), Shabda (शब्द), Sparsha (स्पर्श) conveying human senses as vision, taste, smell, sound and touch respectively. Also to explain the nature of periodicity that is involved in the evolutionary system as continuum of progressive evolutions and in the nature of changes that are involved in transit from one phase to next in succession following the evolutionary process that is involved in the system of evolution of numbers in square continuum which has been explained before. The illustration of gradual changes from seedling to leaf development, to flowering, to generation of fruits and finally to seed as the cause for next evolution is relevant which has been explained in these Darshanas.

The clarifications which have been put forward while explaining the various aspects of distinguishableness and indistinguishableness; and identicals and different, have been finally so quantitatively dealt with, that those very deductions which formed the basis of evolution of continuum of numbers also formed the foundation of fundamental unit and digits in association, in which the intensities of fundamental one and the digits in successive phases of unit, 10, 100 and so on, must vary in opposite directions following the unique continuum of increasing magnitudes of intensities of derived phases. Following this approach the concept of one un-associated with anything or for that matter any digit starting with

one of nil magnitude and the concept of nil as 0 were also perfected. This continuum of numbers has been through the millenniums formed the basis in the evolution of numerical magnitudes in science. It is however, difficult for one to understand this particular aspect from the available interpretations of the original Sutras of Vaisheshik Darsana that are available now-a-days. The Sutras are really meant to convey the various quantitative significances and aspects of the universal law. But the interpretations by subsequent authors have conveyed those significances by applying those through other derived concepts; for example these were applied to explain the various significance of Gods, Atman, in their different manifestations like the thermodynamic phases. One thing is however clear that the concepts behind these ancient postulates of the universal wave as well as the present theory of unified field continuum strictly are in agreement/similar with the sutras of Vaisheshik Darsanas.

(6) Relationship of Numerical Continuum with Square Continuum

We have discussed before about what could be the various factors that led to the adoption of 0 and only 9 digits in the continuum of numbers as multiple of 10. We have also shown that the 9 digits have direct relationship with regular tetrahedral evolutionary configuration in an isotropic evolution in 4 directions; and that in a 4 directional evolutionary wave there are 5 tetrahedra which have 25 cognisable positions. We have also shown that a plane square continuum is a direct translation of this unit universal wave into a plane having the configuration of square. If we take a square configuration in a plane and make this up of 25 numbers of identical square units, then that unit square of 25 would represent the unit wave as shown in the square configuration of fig. 13.

Quantitative explanation of this can be directly deduced from one unit of the tetrahedral configuration of the universal wave continuum. The configuration of the

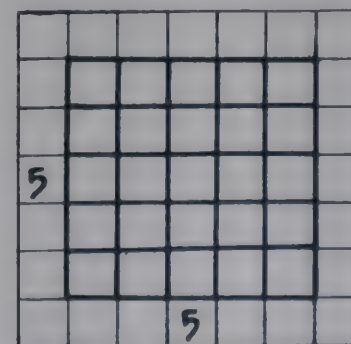


Fig. 13

unit wave consists of 5 regular tetrahedra in which 4 are associated face to face with a central one. In order to realise the quantitative significance of the various dimensions involved in a regular tetrahedron as well as in the assembly of 5 making one unit wave, one would have to know the relative distance between significant positions in the configuration. This aspect has been discussed in detail elsewhere.* In the following for the sake of ready reference magnitudes of these important relationships have been mentioned:

The distance between the centre of any triangular face and the centroid of a regular tetrahedron has been taken as the unit of distance here. All the distances have been calculated below in terms of this unit. The magnitudes of the other significant dimensions of the tetrahedron, expressed in this unit are as follows:

1. Centre of tetrahedron to centre of triangular face = 1
2. Centre to mid side = $\sqrt{3}$
3. Centre to corner of tetrahedron = 3
4. Altitude = 4
5. Mid triangular face to corner = $2\sqrt{3}$
6. Mid triangular face to any mid side of the same face = $\sqrt{2}$
7. Median of any triangular face = $3\sqrt{2}$
8. Side of tetrahedron = $2\sqrt{2}\sqrt{3}$
9. Distance between centre of two opposite sides = $2\sqrt{3}$
10. Area of one triangular face = $2 \times 3\sqrt{3}$
11. Volume of one quadrant (equilateral triangular pyramid between centre of 1/4th of tetrahedron and one triangular face) the total vol. of tetrahedron) = $2\sqrt{3}$ (i.e. $1/4$ th of total vol. of tetrahedron)

Since the distance from centre of tetrahedron to centre of any triangular face is 1 and the altitude which is the distance from centre of any triangular face to the opposite corner of the tetrahedron is 4, then when one tetrahedron is placed face to face against the central one, the distance between the centre of the central tetrahedron to the corner of the second or attached tetrahedron would be 5. Thus in the unit universal wave the mid centres of the triangular faces of central tetrahedron are at unit distances from the centre of the unit wave which is also the centre of the central tetrahedron. The boundary or

apical or corner positions of the associated tetrahedra would be at a distance of $4+1=5$ from the centre of the unit wave and whose diameter would be 10.

We have already explained that a square is a configuration in a plane derived from a regular tetrahedron when placed vertically on one edge, with the centroid coming directly above. With the stated convention about the unit of length in which the distance from the centre of the tetrahedron to mid triangular face is one, the magnitude of sides of projected square would have magnitude of $2\sqrt{3}$ which is the same as the distance between the mid points of any two pairs of opposite sides of tetrahedron of unit magnitude. In the projected square unit this distance $2\sqrt{3}$ becomes the sides of the unit square. The diagonals of the unit square retain the same magnitude of sides of the tetrahedron. The area of the square would be $2\sqrt{3} \times 2\sqrt{3} = 12$ square units. Thus one can justifiably say that the projected unit square having magnitude of 12 sq. units represent the central tetrahedron of the unit universal wave (see fig 14).

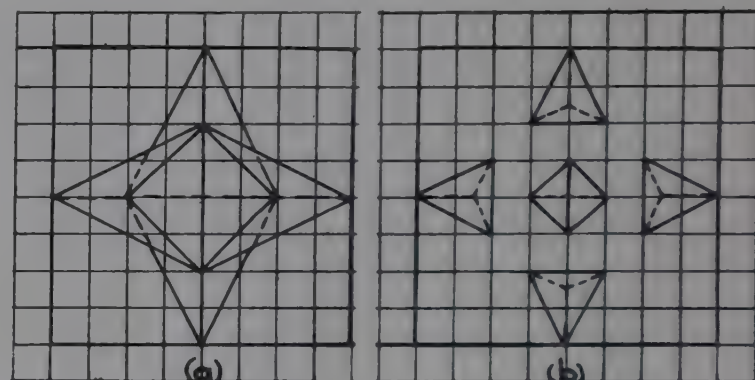


Fig. 14—Unit Universal Wave

The boundary of the tetrahedron has 4 apical positions of the 4 tetrahedra each at a distance of 5 from the centre of the unit wave. If a tetrahedron is constructed with these four positions as the centres of the triangular faces, then the relevant magnitudes of that tetrahedron would be as follows:

The centre to mid triangular face would be 5×1

The magnitude of the side of the square when projected at a plane would be $5 \times 2\sqrt{3}$

The area of the projected square on this tetrahedron would be $5 \times 2\sqrt{3} \times 5 \times 2\sqrt{3} = 25 \times 12$.

* Geometry of Space-Time Configuration in the Light of the Theory of Universal Spherical Wave of the Energy Field of the Universe and Atom, *Technol.* 3 (4), (1966).

The unit configuration thus obtained can be re-presented in a square continuum of individual squares each consisting of 25 square units.

(7) Digits and Numbers from Square Continuum

A continuum of squares, each consisting of 25 units has been presented in fig. 15. Starting from O, a point of position the progressive increase of magnitudes of the diagonals (which is the hypotenuse of right angled isosceles triangles) would progressively vary as 1, 2, 3, 4, 5, 4, 3, 2, 1 ending up into a point of position at O_1 the corner point of position opposite to the starting point O. The number of finite diagonals is only 9 and no more. In such a continuum of squares of unit universal waves each unit wave has 9 diagonals of finite magnitudes preceded as well as followed by a point position at which diagonal has zero magnitude. If the diagonals will be ascribed relative magnitudes then progressively increasing magnitudes of diagonals in the continuum will have their relative magnitudes as 1, 2, 3, 4, 5, 6, 7, 8, 9, as shown in the fig. 15. The actual magnitudes of these however relative to the sides of the square as units will be products of these digits and $\sqrt{2}$. The magnitude of diagonal next to 9 is diagonal of magnitude 10 which passes through the critical point O_1 of the first square of 25 units. In this, it may be seen that the magnitudes of the diagonals alternately are indivisible and divisible into exact halves giving rise to odd and even digits. At the magnitude 10, the diagonal passes through O_1 and has two equal halves of 5 each on either side. With further increase of magnitude of diagonals, a new phase starts from O_1 varying in magnitudes to O_2 , in which the portion of the diagonals outside this new phase continues to remain constant as $5+5=10$ till the diagonal passes through O_2 when the magnitude of diagonal becomes $10+10$. Similarly the magnitude of the diagonals increases from 20 at O_2 , to 30 at O_3 from which a third phase develops between O_2 to O_3 . The mode of increase of magnitude of the diagonals and the development of new phases are: from 0 to 10 (of 9 magnitudes) in the unit phase between O and O_1 ; between 10 to 20 in the tenth phase between O_1 and O_2 ; 20 to 30 in the 20th phase between O_2 and O_3 and so on. In the manner described in the above, the diagonals in the continuum thus increase in their magnitudes while the diagonals in the unit squares of 25 vary from minimum through maximum to minimum and the process goes on repeating in unit waves of 25 in succession.

The picture one obtains about numerical evolution from fig. 5 is identical in significance with the evolution of thermodynamic phases illustrated in fig. 2. In fig. 2 as

the intensity of energy of space decreases i.e. while the space magnitude increases, the intensities of the different material phases vary from minimum through maximum towards minimum while new phases develop in sequence. The phases as space, gas, liquid, solid correspond to variations of condensed phases as 1, 2, 3, 4, 5, 4, 3, 2, 1 and surrounded by depleting intensities of 1 in phase characteristics of unit 10, 20, as $1/1$, $1/10$, $1/20$

Exactly similar variations have been observed to be applicable to elementary atomic matter evolution in equilibrium with space as energy; intensive properties of elementary atoms vary through inertial co-ordinates from minimum to maximum and maximum to minimum, while space energy intensities decrease in continuity with constant gradient.

The realisation of mechanism of change from one phase to another in succession through the critical states forms the most fundamental significance in the establishment of continuum; of one of fundamental and the other derived in succession; one is continuous, the other is discontinuous varying in sequence through minimum, maximum and minimum. The nature of variation of matter intensities in atoms in periodic system, which has been explained in other works* follows maximum minimum pattern which has been experienced from modern scientific investigations but the nature of variation of space magnitudes representing energy intensities which should be in equilibrium in evolutionary context with atomic matter in their periodic classification has yet to be fully realised through experiments.

Relationship of the diagonals, with progressively increasing magnitudes of squares, follows the same pattern as will be obvious from fig. 15, viz. for squares $1^2, 2^2, 3^2, 4^2 \dots$ (sides as 1, 2, 3, 4....) the magnitudes of squares on the diagonals (of squares $1^2, 2^2, 3^2, 4^2 \dots$) are as $2.1^2, 2.2^2, 2.3^2, \dots$. Thus the progressively increasing magnitude of the diagonals are $\sqrt{2.1}, \sqrt{2.2}, \sqrt{2.3} \dots$. It is also clear from fig. 12 that as the magnitudes of squares in terms of equivalent number of unit squares increase in the continuum as 1 square unit, 2 square units, 3 square units.... the magnitudes of diagonals expressed in terms of square units increase as 1, 2, 3, 4, 5..... and the diagonals as such as $\sqrt{1}, \sqrt{2}, \sqrt{3}, \sqrt{4}$.

Therefore in a square continuum of identical units, of squares, the application of the formula

$$X/Y(Y^2+2Y+1)$$

* Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol.* 5 (2A) (1968)

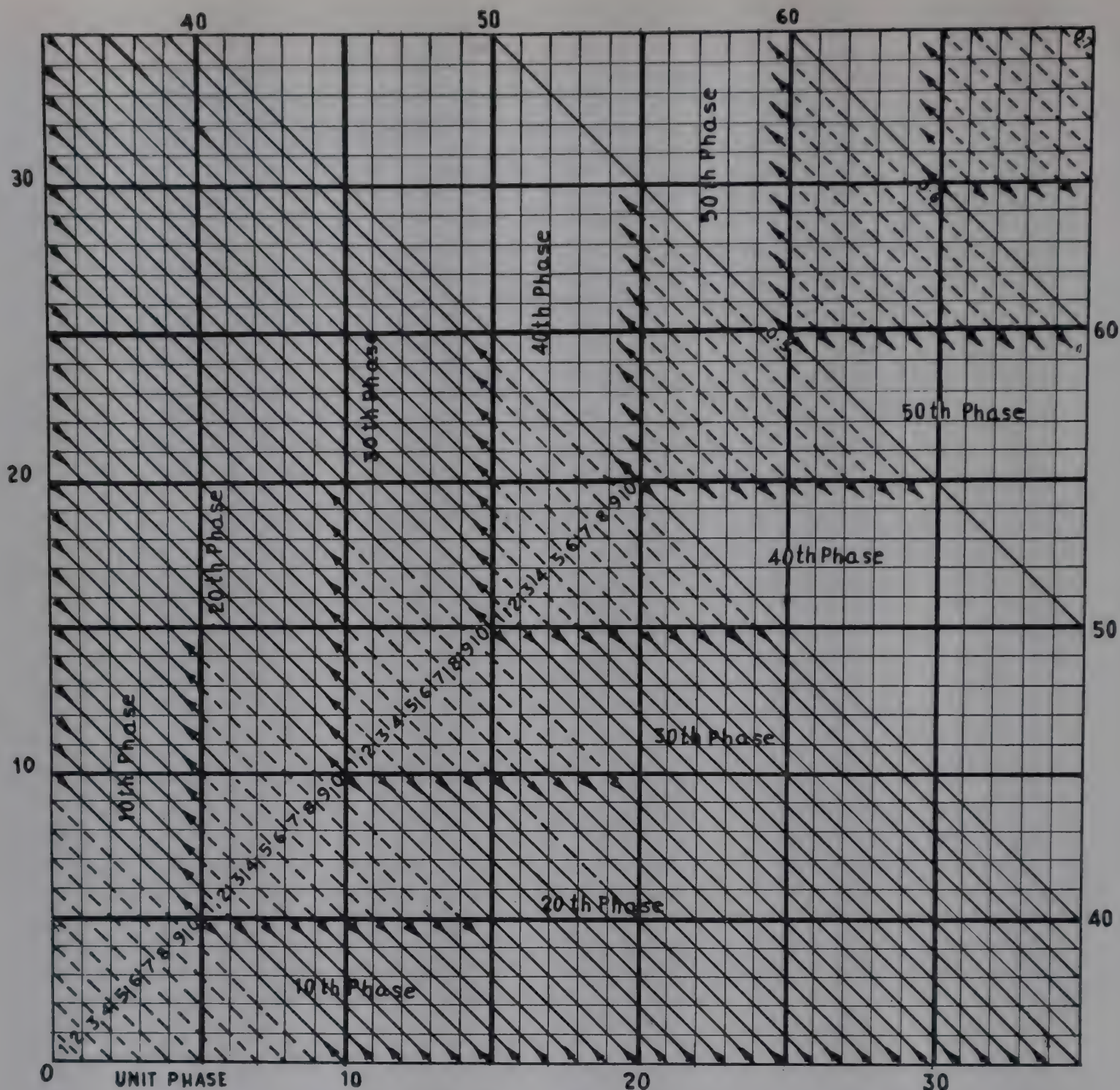


Fig. 15—Square Continuum in the Background of Plane Surface

would give the configuration of increasing magnitudes of perfect squares in one direction which has been explained before. Since X/Y in the continuum would be always 1, inserting the value of Y as 0, 1, 2, 3 it would give the magnitudes of squares as 1^2 , 2^2 , 3^2In terms of square units the series would be as 1, 4, 9, 16, 25.....

The above results, can be summarised as follows:

(1) If the magnitude of numbers would be expressed in terms of squares as 1^2 , 2^2 , 3^2then the square continuum in terms of square units would comprise the discrete series 1, 4, 9, 16.....in one direction.

(2) If it would be in terms of side of squares the continuum would comprise 1, 2, 3, 4.....in one direction.

(3) If it would be in terms of diagonals of the squares the continuum would comprise $\sqrt{2.1}$, $\sqrt{2.2}$, $\sqrt{2.3}$, $\sqrt{2.4}$ in one direction.

(4) If the increasing square magnitudes in the continuum would be in terms of number of square units then squares on diagonals in terms of number of square units would be 1, 2, 3....and the diagonals (which would have significance of sides) themselves would be as $\sqrt{1}$, $\sqrt{2}$, $\sqrt{3}$Thus if the continuum is of increasing magnitudes of squares as 1^2 , 2^2 , 3^2in terms of square units would be as 1, 4, 9....; if the increasing magnitudes of squares are in terms of numbers of square units as 1, 2, 3....the increasing magnitudes of sides are as $\sqrt{1}$, $\sqrt{2}$, $\sqrt{3}$

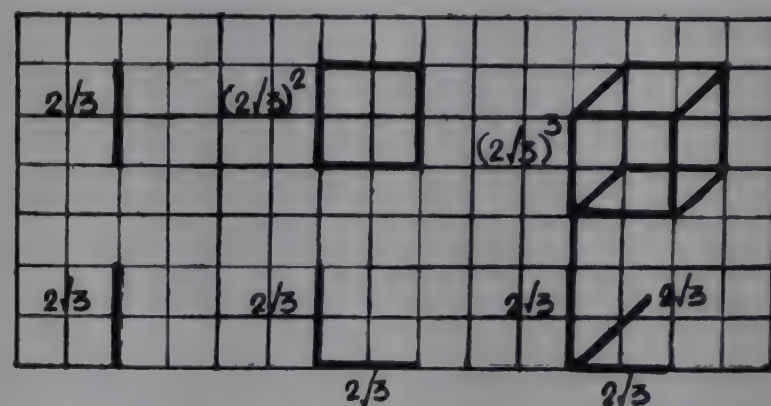
CHAPTER 4

Multidimensional Configurations

(1) Multi-dimensional (directional) Continuum

The anomaly in the two conventional terms “direction” and “dimension” has been discussed in the previous works. In dimensional analysis, dimensions refer to various different aspects of configuration or different factors causing a phenomenal existence. The direction is one which indicates the course of change in the continuum.

About the magnitudes in unidirectional (linear), two directional (square), or three directional (cubic) continuum, significance of general configurational aspects is more or less clear, whereas the true nature and the significance of 4 dimensional continuum are not clear. Magnitudes of linear, square or cubic continuum are normally derived from the relationship that are obtained in the configuration of square in a plane continuum. Thus when a square is derived from projection of a regular tetrahedron of unit magnitude on a plane as mentioned before, the magnitude of side of the square is $2\sqrt{3}$ assuming that the unit magnitude of distance as the distance between centre of the unit tetrahedron and centre of the plane triangular faces. Thus we can use this magnitude as the unit of linear magnitude of distance in a plane. We can employ this to measuring linear magnitudes with respect to this unit $2\sqrt{3}$ in linear, square as well as in cubic continuum. This is explained in fig. 16.



Unidirectional Two directional Three directional
Fig. 16

It should be noted that the magnitude $2\sqrt{3}$ of the sides of the square and the cube generated from the unit tetrahedron, in terms of unit magnitude of sides of cube is $2\sqrt{3}$. Particular significance of $2\sqrt{3}$ in the different cases will be explained later in the discussions on 4 dimensional co-ordinates.

(2) Significance of 4 Dimensional Continuum

A significant aspect which needs to be mentioned here is that the linear, square and cubic configurations described in the above are based on projection of complete configuration of a generated tetrahedron. The dimensions projected are all outlines or sides of the completed tetrahedral configuration which has attained constancy in magnitude of 1 unit. These continua are generated from addition and multiplication of constant unit $2\sqrt{3}$. These continua therefore are not applicable to a process of creation or emanation of configurations in which the magnitude of configuration changes as well as the magnitude of the unit.

The tetrahedral evolution, as has been described in the theory of universal wave, is the wave of creation of configuration, evolution of continuously changing phenomenal universe starting from something from an imaginary point of position which emanates in perfect isotropy in 4 regular tetrahedral directions. These directions are obviously radial from the emanating point source of position. But one has to make sure whether these 4 directions are the same kind of directions as is conventionally understood and as has been explained

Increasing magnitudes in linear continuum	Increasing magnitudes in square continuum	Increasing magnitudes in cubic continuum
$1.(1.2\sqrt{3})^1$	$1.(1.2\sqrt{3})^2$	$1.(1.2\sqrt{3})^3$
$1.(2.2\sqrt{3})^1$	$1.(2.2\sqrt{3})^2$	$1.(2.2\sqrt{3})^3$
$1.(3.2\sqrt{3})^1$	$1.(3.2\sqrt{3})^2$	$1.(3.2\sqrt{3})^3$
$1.(4.2\sqrt{3})^1$	$1.(4.2\sqrt{3})^2$	$1.(4.2\sqrt{3})^3$

It may be seen that the increasing magnitudes of line, square and cube in their respective continuum are in terms of multiples and powers of the unit $2\sqrt{3}$ as side having only linear dimensional (directional) significance.

before for linear, square continuum or cubic. In these, directions are linear in concept. In a regular tetrahedron of unit magnitude the distance from centre to the corner is 3. If the 4 directions would be from centre to four corners, the magnitude of each radial would have been 3 for each linear direction (each direction having unit magnitude). But the volume of each triangular pyramid (one quadrant) towards one triangular face has also a unit magnitude of $2\sqrt{3}$ on the same premise. There are 4 such identical (inertial) quadrants through which emanation proceeds. The $2\sqrt{3}$ magnitude of volume of each quadrant is incident on each one of triangular plane surface face whose area is $2 \times 3\sqrt{3}$ on the same premise. The product of these two dimensions for each quadrant is $4 \times 3 \times 3$ and the sum total for 4 quadrants is $16 \times 3 \times 3$.

The magnitude $2\sqrt{3}$ in the tetrahedral 4 directional evolution is very significant. This $2\sqrt{3}$ in this particular case has 3 directional possibilities (having the dimensions of volume) and is incident on the triangular plane surface face of each quadrant in 4 isotropic directions; the area of triangular surface face is 2 directional. This concept of 4 dimensional continuum is entirely different from the nature of increase of magnitudes of continuum in one, two or three directional rectangular co-ordinates as linear, square and cubic continuum in which directions are linear. The significance of $2\sqrt{3}$ in this case is something like intensity as pressure or density having 3 directional probability and the effect of these can be realised at the triangular surface normal to the direction of emanation giving rise to a phenomenon like force. The magnitude $4 \times 3 \times 3$ for each quadrant thus represents the total force for one quadrant and the 4 quadrants will have total force of $16 \times 3 \times 3$.

In fig. 17 ABCD is a regular tetrahedron, O is the centroid. The equilateral triangular pyramid OABC is one quadrant, OBCD second quadrant, AOCD third quadrant, OABD fourth quadrant; the volume of each quadrant is $2\sqrt{3}$. The area of each of the triangular faces ABC, BCD, ACD, ABD, is $2 \times 3\sqrt{3}$.

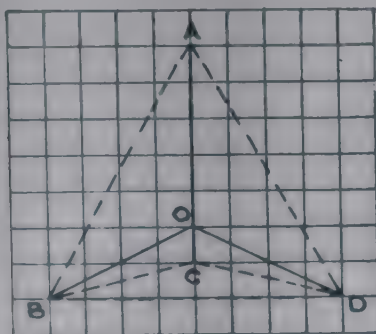


Fig. 17

If we treat this three dimensional $2\sqrt{3}$ as one direction—then keeping similarity with linear increase of magnitudes as $1(2\sqrt{3})^1$, square as $1(2\sqrt{3})^2$ and cubic as $1(2\sqrt{3})^3$, in tetrahedral or 4 directional measures it would be $1(2\sqrt{3})^4$. But $1(2\sqrt{3})^4 = 16 \times 3 \times 3$ which is the same as the product of $2\sqrt{3}$ and area $4.2.3\sqrt{3}$ of four triangular surfaces of the tetrahedron as has been shown before.

It would appear from this that product of increasing magnitudes of a quadrant and area of triangular faces would give the increasing magnitudes of directions in tetrahedral i.e. 4 directional evolution. Thus, increasing magnitudes in tetrahedral evolution would be:—

$$1^2.8.3\sqrt{3} \times 1^3.2\sqrt{3}$$

$$2^2.8.3\sqrt{3} \times 2^3.2\sqrt{3}$$

$$3^2.8.3\sqrt{3} \times 3^3.2\sqrt{3}$$

On rearranging this becomes:

$$1. (1.2\sqrt{3})^4$$

$$2. (2.2\sqrt{3})^4$$

$$3. (3.2\sqrt{3})^4$$

Comparing this with the corresponding magnitudes in one, two and three dimensional cases, it would be clear that, though in all the 4 cases of evolutionary continuum—linear, square, cubic and tetrahedral, the increase in magnitude of $2\sqrt{3}$ is involved, in terms of power of directions in all the cases; the first three cases have different significance from the 4th case, in the nature of their increase of magnitudes in the continuum besides the magnitudes of powers of the directions involved in the continuum. The significant difference between the first three and the fourth however lies in the fact that in the first three cases the magnitudes of unit has not changed. In these 1 has been retained as 1, whereas in 4 directional continuum not only the magnitude 1 in the continuum changes, but also the magnitude of unit changes as 1, 2, 3,

The difference between the conventional linear, square and cubic co-ordinates and the tetrahedral would thus be found in the above analysis. The magnitude of configuration in the one, two and three dimensional continua increases while the magnitude of unit retains constancy, whereas in the 4 directional continuum the magnitude of configuration changes along with simultaneous change of magnitude of unit also.

In the first three cases the directions are linear; in the 4 directional continuum the direction has pyramidal or cone form (three directional).

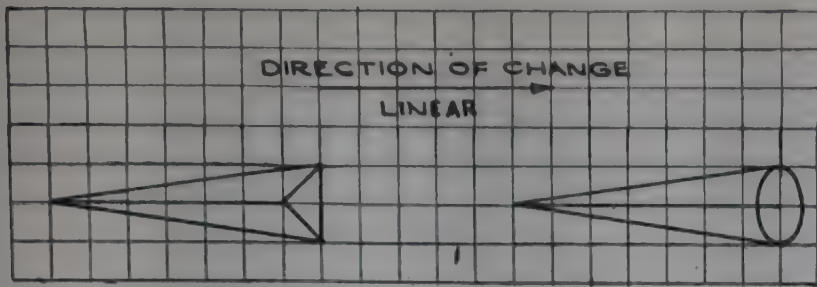


Fig. 18—Direction of Change in 4 Dimensional Continuum

In 4 Directional continuum, each direction occurs from 3 directional something possessing certain intensity having its effect on a two directional plane surface (or 3 directional curved surface if that could be the case), created by it in the way of propagation. Linear direction does not incorporate such concept; in that mode, whatever is in motion the magnitude of that unit is supposed to remain constant and does not undergo change in the subsequent events where results could be perceived as a cumulative effect as power or multiple of that constant unit. In 4 dimensional continuum the emanator having 3 dimensional significance, while emanating, increases in its space time magnitude, the direction having a configuration of opening cone and its intensity decreases in its progressively increasing magnitude of its unit. Four dimensional emanation thus is the concept of accelerated variation of magnitude. In linear direction the change of intensity of unit in the increasing magnitude of the continuum does not occur. This is the crux of the problem.

Intensities of Energy in Sun's and Earth's Atmospheric Space

As an illustration of this the characteristics of space on the surface of the sun can be compared with the characteristics of space in the earth's atmosphere. One meter cube of space on the sun's surface has energy intensity which is many times the energy intensity of one m^3 of space at the earth's atmosphere. If one m^3 of space at the sun's surface would be converted into space corresponding to earth's atmosphere, it will be a volume of space of earth's atmosphere which would be many times one meter cube. The difference can be expressed in two ways. We can say that the magnitudes of unit space is different at the two locations or it can be expressed as the intensities expressed as energy content of space per unit volume (if the magnitude of unit would remain constant) would be different at the two locations. Both however would convey the same significance.

(3) Two Important Significances

The nature of continuum and change of magnitudes

that occur progressively in the continuum would reveal certain other consequences of far reaching importance. Let us write down for comparative analysis the magnitudes in the various continuum as discussed before:

One dimensional	Two dimensional	Three dimensional	Four dimensional
Linear continuum	Square continuum	Cubic continuum	Tetrahedral continuum
$1.(1.2\sqrt{3})^1$	$1.(1.2\sqrt{3})^2$	$1.(1.2\sqrt{3})^3$	$1.(1.2\sqrt{3})^4$
$1.(2.3\sqrt{3})^1$	$1.(2.2\sqrt{3})^2$	$1.(2.2\sqrt{3})^3$	$2.(2.2\sqrt{3})^4$
$1.(3.2\sqrt{3})^1$	$1.(3.2\sqrt{3})^2$	$1.(3.2\sqrt{3})^3$	$3.(3.2\sqrt{3})^4$
$1.(4.2\sqrt{3})^1$	$1.(4.2\sqrt{3})^2$	$1.(4.2\sqrt{3})^3$	$4.(4.2\sqrt{3})^4$

The first significance could be derived from analysing the changing magnitudes in the different continuum under *constant power* in direction of decreasing magnitudes towards least. The direction is vertically upward in each column. Second significance is in the horizontal series in the unit state in which the *power decreases*, viz. power varies from highest to least.

Take the second case first in their unit state:

Four dimensional	Three dimensional	Two dimensional	One dimensional	Nil dimensional
$1(1 \times 2\sqrt{3})^4$	$1(1 \times 2\sqrt{3})^3$	$1(1 \times 2\sqrt{3})^2$	$1(1 \times 2\sqrt{3})^1$	$1(1 \times 2\sqrt{3})^0$

Since the series belongs to state of unit, whatever be the power, the magnitude of the state cannot be less than unit. Therefore the portion $(1 \times 2\sqrt{3})^0$ cannot be less than 1; otherwise if it were 0 then 1.0 would be 0, which is not permissible.

Therefore anything to the power 0 should be 1.

On the other hand take the magnitudes in the 4 directional continuum.

$0(0.2\sqrt{3})^4$ state beyond unit state
 $1(1.2\sqrt{3})^4$
 $2(2.2\sqrt{3})^4$
 $3(3.2\sqrt{3})^4$
 $4(4.2\sqrt{3})^4$

As the magnitude is reduced beyond the unit state $1(1 \times 2\sqrt{3})^4$, that state would be $0(0.2\sqrt{3})^4$. Since unit state is the least magnitude conceivable, whatever be the magnitude of $(0 \times 2\sqrt{3})^4$, the product of this and 0 must be also zero. Thus anything multiplied by 0 is zero.

Again take the magnitudes in vertical columns in any continuum. The portion within brackets under any constant power, the magnitude less than unit state is $(0 \times 2\sqrt{3})$. The state again is of nil significance relative to the unit state which also leads to the same conclusion that zero to the power anything is zero. It thus follows that zero multiplied by anything is zero which could have any power or multiplier it would still be zero.

(4) Significance of Power of Dimensions and Configurations of 1, 2, 3, 4, Dimensional Co-ordinates

Let us analyse the configurations of straight line, square, cube etc. assuming the magnitude of lines and sides of the squares and cubes as $2\sqrt{3}$ which has been discussed in a previous section entitled "Multi dimensional (directional) continuum". We have in that section as well as in the subsequent ones emphasised the special significance of the magnitude $2\sqrt{3}$. We shall further elaborate the significance of the multi dimensional co-ordinates of configurations and the relationship of any dimension of the resulting configuration with the power of the co-ordinates. In order to understand the discussions in its proper perspective one must remember the relative magnitudes of various dimensions of unit tetrahedron on the one hand and the magnitudes of dimensions of configurations of cube, square etc. as derived from tetrahedron on the other. Significance of fig. 12 is of particular relevance to the following discussion.

One Dimensional Linear Configuration

Let us take first the concept of line. In order to develop the magnitude of the line in one directional coordinate from a point of position to linear magnitude

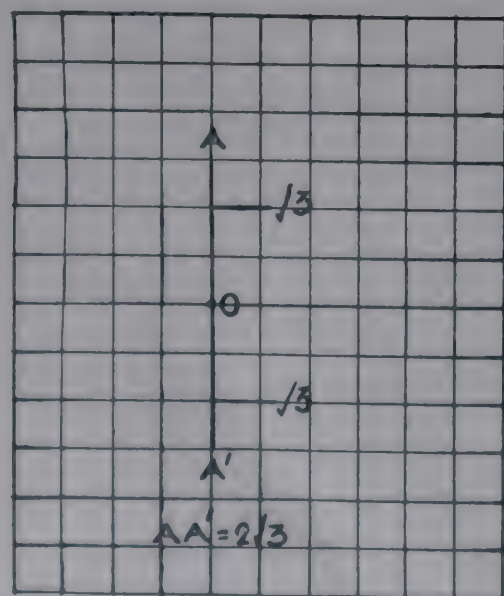


Fig. 19

of $2\sqrt{3}$ let us assume the following explanation. In fig. 19, O is a point of position. O in one straight linear direction 2 linear distances OA and OA' each equal to magnitude of $\sqrt{3}$ will generate the linear magnitude $2\sqrt{3}$. This magnitude of $2\sqrt{3}$ can be expressed as $(2 \times \sqrt{3}) \times 1$, which can also be written as $2 \times \sqrt{3} \cdot \sqrt{1}$.

The linear magnitude of AA' is $2\sqrt{3}$ and can be assumed to have 2 times development of unidirectional linear magnitude of $(\sqrt{3})^1$ in one straight direction or co-ordinate.

Two Dimensional Square Configuration

The generation of the square of side $2\sqrt{3}$ can be assumed to have developed from 2 opposite pairs of 2 linear co-ordinates at right angles to each other making the diagonal of the square BB' (fig. 20). The diagonal BB', which was originally the side of the unit regular tetrahedron from which the square has been projected, has magnitude of $2 \times \sqrt{2}\sqrt{3}$. Similarly assuming the development of the square in a similar manner, the development of the linear magnitude of diagonal BB' from a point of position takes place. The square thus can be assumed to have developed its diagonal $2 \times \sqrt{2}\sqrt{3}$ which can be expressed in terms of linear magnitude $2\sqrt{3}$ of side multiplied by *root of its power* of co-ordinates which is 2. Thus $2 \times \sqrt{3}\sqrt{2}$ can be expressed as $(2\sqrt{3}) \times \text{root of power 2}$, i.e. $2\sqrt{3} \cdot \sqrt{2}$.

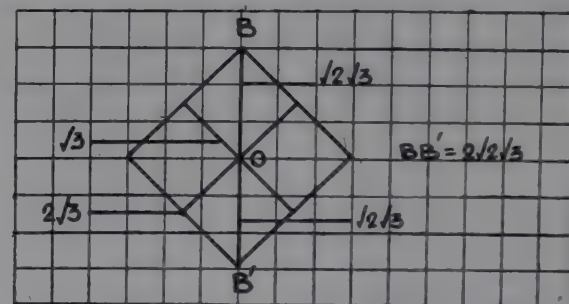


Fig. 20

The concept of the square in terms of its diagonal thus can be recognised as the magnitude of side multiplied by root of power 2. Thus BB' is $2\sqrt{3}\sqrt{2}$.

Three Dimensional Cubic Configuration

Let us take the 3 dimensional case of cubic configuration which represents 3 directional co-ordinates in its configuration. Cubic configuration is one which can be generated from a unit regular tetrahedron when that vibrates in opposite phases with respect to its centre describing 8 positions which form the 8 corners of the cube. Any of the diagonals of the cube has relative magnitude of 6 which can be expressed as 3×2 or $2 \cdot \sqrt{3}\sqrt{3}$ as shown in fig. 21

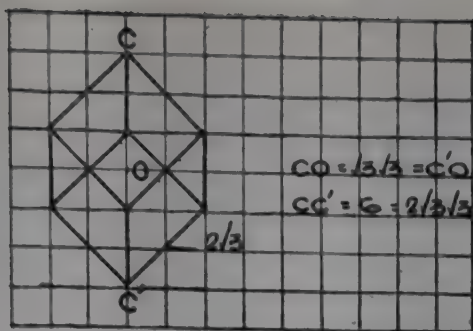


Fig. 21

Thus cube is a three dimensional configuration which can be assumed to have been generated from 2 opposite pairs of three sides in three directions at right angles to one another (which is the same as the 3 axis between opposite square faces through the centre of the cube). The magnitude of side in each direction is $2\sqrt{3}$. Thus if the diagonal of the cube is expressed in terms of $2\sqrt{3}$ (which is the magnitude of the side of the cube) then linear magnitude of the diagonal would be as magnitude of side multiplied by *root of the power which is* $\sqrt{3}$ for 3 dimensional case. The cube can be expressed in terms of its diagonal, linear magnitude of which would be equal to linear magnitude of its side $2\sqrt{3}$ multiplied by $\sqrt{3}$, ($\sqrt{3}$ being root of power 3) for three dimensional configuration. Thus $2\sqrt{3} \times \sqrt{3} = 2 \times 3 = 6$.

Four Dimensional Case

Let us now see what could be the explanation in the case of 4 dimensional configuration. The explanation in tetrahedral mode has been explained before. In the following octahedral mode will be considered. The configuration of octahedron can be generated by unit of regular tetrahedron when that vibrates in opposite phases with respect to the mid-point of the altitude of the tetrahedron.

The octahedron thus generated has the magnitude of distances from the centres of the triangular faces to centre of the octahedron such as one like $MO=2$ (fig. 22). The magnitude of distance 2 in unit tetrahe-

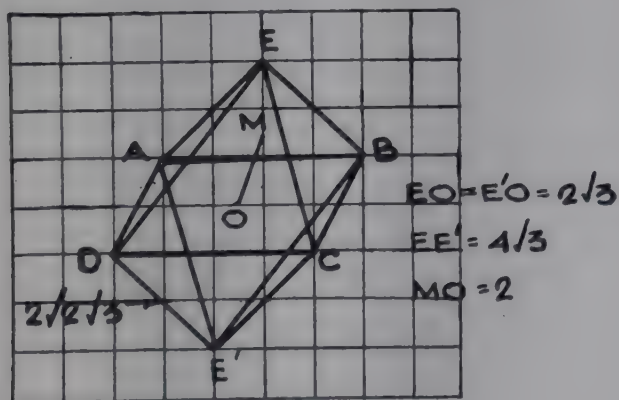


Fig. 22

dral configuration is equal to half of the altitude of the unit tetrahedron. The diagonal of the resulting octahedron EE' is $4\sqrt{3}$. The co-ordinates $EO=E'O$ has magnitude of $2\sqrt{3}$. All the sides of the octahedron have the same magnitude as the sides of the tetrahedron, which is $2\sqrt{3}\sqrt{2}$.

The configuration of octahedron can be considered to be generated from 2 alternative approaches. In the first approach 2 opposite pairs of 4 linear co-ordinates EA, EB, EC, ED and $E'A, E'B, E'C, E'D$ at an angle of 60° to each other generate a square $ABCD$ passing through the centre of the configuration. In the other approach 2 opposite pairs of 4 linear co-ordinates (at 109° between each opposite other) from a point of position, which forms the centre of the configuration, emanate towards centres of 4 opposite pairs of equilateral triangular faces thus generating the configuration of regular octahedron.

If now, like the cases in square and cubic configurations, the octahedron would be represented as linear magnitude by its diagonal, then the magnitude of the diagonal in terms of the distance of the corners to the centre of the octahedron is $2\sqrt{3}$; the linear magnitude of the diagonal in terms of this $2.2\sqrt{3}=4\sqrt{3}$. This in order to be in conformity with the configurations of squares and cubes as explained before, should be $2\sqrt{3} \times \text{root of 4 as power for 4 dimensional case}$. Thus $2\sqrt{3}$ multiplied by $\sqrt{4}=4\sqrt{3}$, which is the linear magnitude of the diagonal of the octahedron generated from a configuration of unit regular tetrahedron vibrating in opposite phases with respect to the mid point of its altitude.

One can now summarise the results in the following in respect of linear presentation of the configurations of one dimensional linear magnitude by a straight line, two directional square magnitude by diagonal of square, three directional cubic magnitude by diagonal of cube and 4 directional octahedral configuration by diagonal of octahedron. The linear magnitudes in these cases are:

- $2\sqrt{3} \times \sqrt{1}$ for one dimensional linear magnitude;
- $2\sqrt{3} \times \sqrt{2}$ for two dimensional square by linear magnitude (2 directional) as diagonal of square:
- $2\sqrt{3} \times \sqrt{3}$ for the 3 dimensional configuration by linear magnitude as diagonal of cube.
- $2\sqrt{3} \times \sqrt{4}$ for the linear magnitude of the diagonal of the 4 dimensional configuration as octahedron.

It may be noticed from the above that $\sqrt{1}$, $\sqrt{2}$, $\sqrt{3}$ and $\sqrt{4}$ are the roots of the powers of dimensions (directions) of co-ordinates involved in the configurations in the respective cases as one, two, three or four dimensional as the case may be. It should be remembered that $\sqrt{3}.\sqrt{4}$ is the distance between mid points of opposite sides of unit tetrahedron.

In this connection reference has to be made to the discussions at fig. 12 about increase of linear magnitudes in terms of magnitudes as numbers of identical square units as one square unit, two square units, three square units....which can be represented by corresponding linear magnitudes as $\sqrt{1}$, $\sqrt{2}$, $\sqrt{3}$, $\sqrt{4}$ From the comparison of the significance of those increasing linear magnitudes and in terms of increasing numbers of square units and the significance derived from the above discussions as:

$$2\sqrt{3} \times \sqrt{1}$$

$$2\sqrt{3} \times \sqrt{2}$$

$$2\sqrt{3} \times \sqrt{3}$$

$$2\sqrt{3} \times \sqrt{4}$$

it can be seen that the increasing magnitudes of the different configurations of continuum as unidimensional, two dimensional, three dimensional etc. will have linear representation involving magnitude which are actually the magnitude of power of the number of dimensional co-ordinates of configuration of the continuum. These two approaches about the concept of magnitude and related with the magnitude of number of dimensional co-ordinates of the continuum are the crux on which depend our appreciations of the difference between the various dimensional continua that are possible and can be conceived of.

To express the magnitudes of these dimensions in terms of spatial content one should be clear about the nature of that magnitude. For example the content of the above dimensions could be expressed in terms of linear dimensions $2\sqrt{3}$ as linear magnitude of certain number of co-ordinates of the configuration depending on whether they are one, two, three or four dimensional case. Thus the magnitudes of contents of these dimensional cases as expressed in terms of $2\sqrt{3}$ are:

$$\text{One directional line } (2\sqrt{3})^1 = 2\sqrt{3}$$

$$\text{Two directional square } (2\sqrt{3})^2 = 4.3$$

$$\text{Three directional cube } (2\sqrt{3})^3 = 8.3\sqrt{3}:$$

$$\text{Four directional spatial content} \\ \text{should be } (2\sqrt{3})^4 = 16.3.3$$

These cases can also be expressed as:

One direction	$2.(\sqrt{2})^0$	$(\sqrt{3})^1$	$= 2\sqrt{3}$
Two „	$2.(\sqrt{2})^2$	$(\sqrt{3})^2$	$= 4.3$
Three „	$2.(\sqrt{2})^4$	$(\sqrt{3})^3$	$= 8.3\sqrt{3}$
Four „	$2.(\sqrt{2})^6$	$(\sqrt{3})^4$	$= 16.3.3$

(5) Presentation of 4 Dimensional Wave Continuum in Square Continuum of Identical Units in Plane

In 4 directional evolution at the unit state i.e. for a unit tetrahedral configuration, the magnitude of 3 dimensional volume of any of the four pyramidal quadrants of regular tetrahedral unit is $2\sqrt{3}$; any equilateral triangular face of the unit tetrahedron is $2 \times 3\sqrt{3}$. The product of these two dimensions for each quadrant is 4×3^2 . For 4 quadrants it is $4^2 \times 3^2$. These two squares, viz. 4^2 and 3^2 or for that matter $\sqrt{2}$ and $\sqrt{3}$ encountered before in 4 dimensional evolution at the unit state should have great consequence, since in the square continuum where the magnitude of units would not change and retain constancy these should be repetitive. Thus $(3^2 + 4^2)$ multiplied by any square magnitude in 4 directions in a plane should form a continuum which would be repetitive of $(3^2 + 4^2)$ as the magnitude of square in the continuum increases. Thus the discrete magnitudes in the continuum would be $(3^2 + 4^2) \times 1^2$, $(3^2 + 4^2) \times 2^2$, $(3^2 + 4^2) \times 3^2$.. which are the same as 5^2 , 10^2 , 15^2 , 20^2 ...

This continuum is of particular interest since it illustrates progressive increase of 4 dimensional magnitudes of universal wave (as square) in a square continuum in a plane in which the unit square retains its magnitude of constancy in the continuum but 5^2 changes as $5^2.1^2$, $5^2.2^2$, $5^2.3^2$

The above can be explained in another way from the different magnitudes of configuration of tetrahedron; one at centre and the other at boundary of unit universal wave. A regular tetrahedron of unit magnitude, which we have defined before, has the distance between mid points of opposite sides as $2\sqrt{3}$. When a unit tetrahedron is projected on a plane to generate a square on the plane, the projected magnitude of square unit from unit magnitude of tetrahedron has also its magnitude of side as $2\sqrt{3}$.

In the unit universal wave the distance between the centre of the tetrahedron and centre of a triangular face of the central tetrahedron is 1 and the distance between the centre of the central tetrahedron and centre of a triangular face of tetrahedron representing the boundary of the configuration of unit universal wave is 5.

The projected square of the central tetrahedron on plane will have magnitude of $1.2\sqrt{3}$ as its side and the projected square of boundary tetrahedron will have $5 \times 2\sqrt{3}$ as the magnitude of its side.

The magnitude of square of the former is $(1.2\sqrt{3})^2$ and of the latter is $(5.2\sqrt{3})^2$.

The unit universal wave, besides the central tetrahedron, consists of altogether 16 tetrahedra (in 4 groups of 4 each) placed face to face with the central one in the configuration of the unit wave. Arrangement of the unit tetrahedron in the unit wave is shown in fig. 23 figuratively for ready reference:

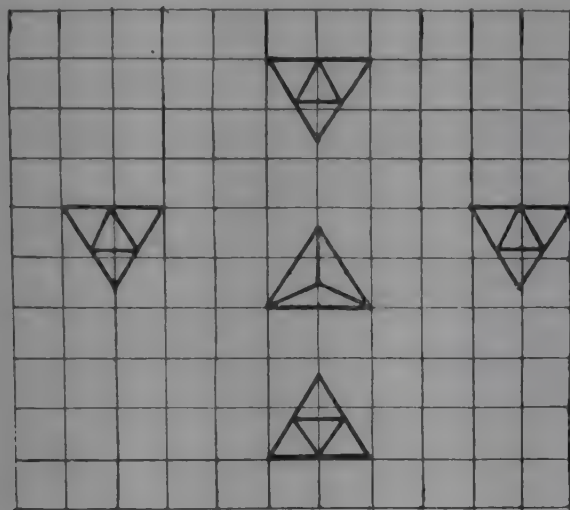


Fig. 23—Simplified Unit Wave of 5

The total area of the square units of the 16 tetrahedra is equal to $16 (2\sqrt{3})^2$ or $4^2 (2\sqrt{3})^2$ and central one is $1(2\sqrt{3})^2$.

But in the configuration of the unit universal wave of the boundary tetrahedron the 16 tetrahedra in association with one central making 17 in total number do not cover all the plane space enclosed with the total space of the boundary tetrahedron whose magnitude is $5^2 (2\sqrt{3})^2$.

The magnitude of intervening vacuum space outside 17 nos. of regular tetrahedral units in the unit wave in terms of projected squares on plane of these 17 units would be:

$$5^2(2\sqrt{3})^2 - [(16.(2\sqrt{3})^2 + 1.(2\sqrt{3})^2)] = 8.(2\sqrt{3})^2$$

Thus to make up the sum total of $5^2(2\sqrt{3})^2$ there are 16 units of square magnitude as $4^2(2\sqrt{3})^2$ and $8.(2\sqrt{3})^2$

as empty space and $1(2\sqrt{3})^2$ for the central tetrahedron; the sum total of these however should be

$$4^2(2\sqrt{3})^2 + 8(2\sqrt{3})^2 + 1(2\sqrt{3})^2 = 5^2(2\sqrt{3})^2$$

Thus we see that a unit universal wave when translated in terms of squares in a plane, the unit magnitude of the wave which is $5^2(2\sqrt{3})^2$ is composed of two parts:

$$4^2(2\sqrt{3})^2 \text{ and } 3^2(2\sqrt{3})^2.$$

If we assume $(2\sqrt{3})^2$ as an unit, then

$$5^2 = 4^2 + 3^2 = (1 + 4 \times 2) + 4 \times 2^2 = (1 + 8) + 16 = 25$$

Distribution of tetrahedral units in the configuration of unit universal wave (fig. 24) would be—

- 1 at the centre (homogeneous zone)
- 8 unrealised tetrahedra as depleted phase in the heterogeneous zone.
- 16 tetrahedra as condensed phase.

Translating these relationships to explain evolution in 4 directions in a square continuum towards progressively increasing magnitudes of the waves in square continuum in a plane will be represented by

$$4(4^2 + 3^2).1^2, 4(4^2 + 3^2).2^2, 4(4^2 + 3^2).3^2 \dots$$

$$\text{or } 4(5^2).1^2, 4(5^2).2^2, 4(5^2).3^2 \dots$$

These magnitudes of number of square units in stages in a square continuum are of great significance in that, these are derived from projection of a tetrahedron on a square plane continuum in the form of unit universal waves of increasing magnitudes in 4 dimensions (directions).

If we assume $5^2(2\sqrt{3})^2$ itself as an unit then the magnitudes of squares in the square continuum in 4 directions reduce to $4.1^2, 4.2^2, 4.3^2 \dots$

The above series representing magnitudes of square units in 4 dimensional evolution realised from 4 dimensional magnitudes in which the unit retains constancy and which is identical with the evolutionary concept of magnitudes in evolution of elementary matter in periodic classification of elements which have been deduced

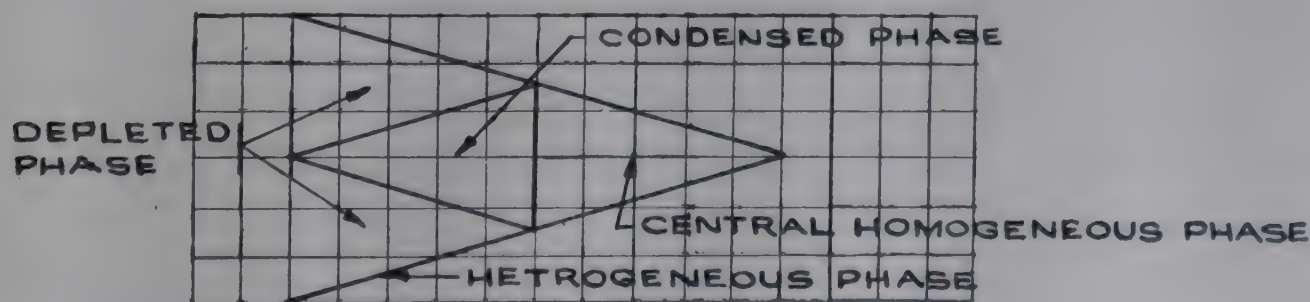


Fig. 24—Unit Wave in one Direction

before in previous works* as $4 \times (Z+1)^2$ where Z can have values 0, 1, 2, 3, 4... The magnitudes in the continuum of periodic classification of elements are $2+2$, $8+8$, $18+18$, $32+32$, which is same as 4, 16, 36, 64....

The evolution and development of magnitudes in course of energy matter evolution is four dimensional in concept. But the magnitudes have been derived from the concept of regular tetrahedron projected as square in a plane continuum of identical square units; as well as from relative magnitudes of various dimensions in the configuration of regular tetrahedron and projected square in plane. The square units in the continuum maintain constancy of magnitude. We also find that in the energy matter evolution the constancy of atomic magnitudes (atoms) as unit of elementary matter in the continuum of periodic classification of elements under conditions of our observation and experience is only apparent. In the universal context however this will not be constant. If magnitudes of atoms would be considered in the universal context, in 4 directional evolution in isotropic regular tetrahedral mode, then it would be found that in the direction of decrease of energy intensity of space, the atomic magnitudes of elementary matter generated in equilibrium will also progressively decrease, resulting in progressive increase of intensity of matter in atomic configuration. Thus one may expect to find regions in space, where the elements normally radioactive on earth's surface (i.e. which are not in equilibrium configuration here) are in equilibrium with that space and be non-radioactive. Conversely, there will be regions, where the matter intensity at equilibrium is less, and where ordinarily stable isotopes (as found on earth) will become unstable and hence radioactive.

(6) Further Elaboration of One, Two, Three, and Four Dimensional Cases

The significant aspects of one or two or three dimensional cases in terms of their magnitudes of contents as straight line, area, volume etc. are more or less amenable to conception and understanding.

Difficulty however arises for understanding of a perspective explanation for 4 dimensional case. The conventional understanding explains that a 4 dimensional case is one in which there are 3 (1.2.3) dimensions of space and one dimension of time. However, in the present

approach this is not acceptable because the time concept and space concept in conventional approach have no direct configurational relationship since one is co-ordinate of inanimate space, the other dimension time is a concept of interval between two events determined by apparatus or agency which is not part and parcel of the configuration. In the present approach all the 4 dimensional cases reveal that in any configuration space and time are part and parcel of the configuration. If one signifies radial direction, other will signify the orbital direction which is the opposite of the first. If space L has the tendency to emanate from a point of position, time T will have direction of contracting the space towards the point of position by decreasing the orbit. Suppose from a point source emanation occurs and takes the form of an opening cone, then with increase of L the orbit of the opening cone will progressively increase. From the opened cone (space) the dimension time would converge towards a point of position, again forming the shape of a cone. First case was however from one to 4 (tetrahedral from its centre), the second case is applicable to evolved configuration of tetrahedron of 4 identical positions. In the latter case time converges 3 to one position of the emerged tetrahedron.

Suppose from a point of position emanation occurs in all directions; it can occur in the shape of 4 tetrahedral directions. The emanation may be accompanied by simultaneous vibration of the tetrahedron in opposite phases making the configuration of cubic, octahedron etc. In the present approach the 1, 2, 3, dimensional configurations are static whereas the 4 directional cases are dynamic. The process of motion such as emanation from a point of position or contraction towards a point of position are involved in radial and orbital motion and can be of continuous type or it can be intermittent, i.e. vibrating between opposite phases during emanation. In the dimensional expressions in the 1, 2, 3 dimensional cases, as line, square, cube, the numerical magnitudes of line and sides of these configurations have linear significance. This magnitude is $2\sqrt{3}$ which has been derived from regular unit tetrahedron as discussed before. Applying this the numerical magnitude of unidimensional line is $2\sqrt{3}$, two dimensional square is $(2\sqrt{3})^2$ and three dimensional cube is $(2\sqrt{3})^3$. In conformity with these, the expression in 4 dimensional magnitude should be $(2\sqrt{3})^4 = 2\sqrt{3} \times 2\sqrt{3} \times 2\sqrt{3} \times 2\sqrt{3} = 16 \times 3 \times 3$. The main problem in this expression is what should be the dimensional significance of $2\sqrt{3}$ in this particular case. Analysis of the magnitudes of various dimensions would throw some light.

We have already shown in a previous section that

* Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol.* 5(2A) (1968)

in 4 dimensional configuration (tetrahedral co-ordinates) the 4 triangular pyramidal directions from the centre of the tetrahedron occurs with variation of volumes of each pyramidal quadrant of the tetrahedron; actually the magnitude $2\sqrt{3}$ is also the numerical magnitude of volume of each triangular pyramidal quadrant of unit tetrahedron. The volume of 4 quadrants is $8\sqrt{3}$. Thus the change involving 4 dimensional co-ordinate involves the change of volume of each quadrant of the unit tetrahedron in terms of $2\sqrt{3}$. In the process of progressive change, each triangular face increases in magnitude of area. The original volume of each quadrant of unit tetrahedron which contained three dimensional magnitude of volume as $2\sqrt{3}$, and which is undergoing also change, then during the process of change this volume as well as the area of triangular faces progressively increases. Volume changes as $(2\sqrt{3}) \times (x)^3$ and area of triangular face increases as $2.3\sqrt{3}(x)^2$.

The significant point which should be noted is that the numerical magnitude of volume of each quadrant of unit tetrahedron is $2\sqrt{3}$ (which is three dimensional). The numerical magnitude $2.3\sqrt{3}$ which is area of each triangular face has two dimensional significance and for 4 triangular faces the magnitude would be $8.3\sqrt{3}$. This very magnitude could be three dimensional, when this would represent volume of cube, since $8.3\sqrt{3} = (2\sqrt{3})^3$; $2\sqrt{3}$ in that case would be linear as side of the cube. Now the associated volume $2\sqrt{3}(x)^3$ and triangular face area $2.3\sqrt{3}(x)^2$ of each quadrant of tetrahedron is $2\sqrt{3}$. $2.3\sqrt{3}(x)^5$. For 4 quadrants this is $4.2\sqrt{3}$. $2.3\sqrt{3}(x)^5$. For unit magnitude of tetrahedron this is $16.3.3$ or $(2\sqrt{3})^4$ and for varying magnitudes of tetrahedron this is $1.(1.2\sqrt{3})^3$, $2.(2.2\sqrt{3})^4$, $3.(3.2\sqrt{3})^4 \dots$ when $x=1, 2, 3 \dots$ respectively.

Suppose that in a unit tetrahedron the magnitude $2\sqrt{3}$, which is the volume of each pyramidal quadrant of the tetrahedron having area of each triangular face as $2 \times 3\sqrt{3}$, will not increase its content while the configuration will increase. The idea is that the content $2\sqrt{3}$ was certain quantity of say energy like entity which was concentrated in a unit tetrahedron as the starting state of emanation. As the configuration of emanation i.e. magnitude of the configuration of the tetrahedron progressively increases the content of the emanating entity as $2\sqrt{3}$ will also get inflated in the configuration and will progressively get reduced in intensity as the magnitude of the configuration of the tetrahedron will increase. As a result while each triangular face area will progressively increase as $1^2 \times 2 \times 3\sqrt{3}$, $2^2 \times 2 \times 3\sqrt{3}$, $3^2 \times 2 \times 3\sqrt{3} \dots$ the volume of each triangular pyramidal quadrant of the tetrahedron will progressively increase as $1^3 2\sqrt{3}$, $2^3 2\sqrt{3}$, $3^3 2\sqrt{3} \dots$

The original content of the emanating entity with increase of volume progressively will get depleted in intensity as

$$\frac{2\sqrt{3}}{1}, \frac{2\sqrt{3}}{2^3}, \frac{2\sqrt{3}}{3^3}, \frac{2\sqrt{3}}{4^3} \dots$$

Thus as the configuration of the tetrahedron will progressively increase, the intensity of the emanating entity starting from $2\sqrt{3}$ will progressively get depleted

$$\text{as } \frac{2\sqrt{3}}{1^3}, \frac{2\sqrt{3}}{2^3}, \frac{2\sqrt{3}}{3^3} \dots \text{and thus progressively depleting}$$

intensity of $2\sqrt{3}$ will react with the progressively increasing area of the triangular faces of the increasing configuration of the tetrahedron. Thus the reaction at the 4 progressively increasing triangular faces of the increasing magnitudes of the tetrahedra will be as follows:

$$[(1^2 \times 2 \times 3\sqrt{3}) \times \frac{2\sqrt{3}}{1^3}] 4 = 1^2 \frac{(2\sqrt{3})^4}{1^3}$$

$$[(2^2 \times 2 \times 3\sqrt{3}) \times \frac{2\sqrt{3}}{2^3}] 4 = 2^2 \frac{(2\sqrt{3})^4}{2^3}$$

$$[(3^2 \times 2 \times 3\sqrt{3}) \times \frac{2\sqrt{3}}{3^3}] 4 = 3^2 \frac{(2\sqrt{3})^4}{3^3}$$

$$[(4^2 \times 2 \times 3\sqrt{3}) \times \frac{2\sqrt{3}}{4^3}] 4 = 4^2 \frac{(2\sqrt{3})^4}{4^3}$$

The product of these two is dimensionally equivalent to that of force since $2\sqrt{3}$ divided by 1^3 is intensity and $1 \times 2 \times 3\sqrt{3}$ is area at which the intensity of the emanating entity will be incident. Thus as the triangular face area progressively increases the resultant dimension as the product of the two (area $\times$ intensity) would progressively vary as follows:

$$\frac{(2\sqrt{3})^4}{1}, \frac{(2\sqrt{3})^4}{2}, \frac{(2\sqrt{3})^4}{3}, \frac{(2\sqrt{3})^4}{4} \dots$$

This would clearly show that an emanating entity as radiation or energy while undergoing emanation in a tetrahedral fashion in tetrahedral co-ordinates with progress of emanation, the force of the intensity of the emanating entity multiplied by the surface on which it will be incident at an instant in its path of emanation will progressively decrease in terms of fourth power of emanating entity.

Comparison of volume surface reaction and intensity surface reaction brings out one very significant aspect mainly:

$$1. (1.2\sqrt{3})^4 \dots \frac{(2\sqrt{3})^4}{1}$$

$$2. (2.2\sqrt{3})^4 \dots \frac{(2\sqrt{3})^4}{2}$$

$$3. (3.2\sqrt{3})^4 \dots \frac{(2\sqrt{3})^4}{3}$$

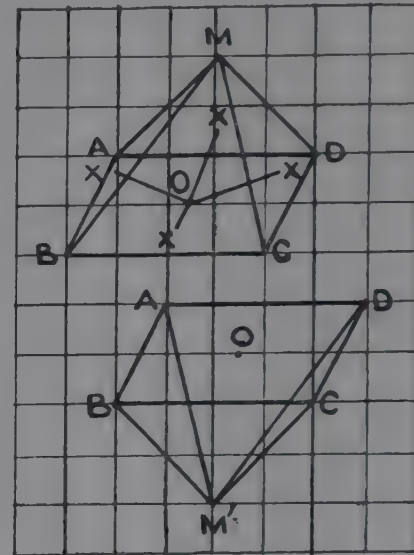
This contradicts $e = \alpha T^4$ (Stefan's Law)
where $\alpha = \text{constant}$.

The change of the configuration occurs at accelerated rate and the change of associated volume and area also becomes accelerated. The thermal radiation for example follows accelerated change of energy intensity as temperature from an emanating point source of heat energy. It follows the 4 power law and is a case in point. This kind of tetrahedral evolution discussed before corresponds to simultaneous change through all four tetrahedral directions.

An alternative case can be considered when $2\sqrt{3}$ would be a linear measure. It would then take the configuration of octahedron and the tetrahedron would not retain its original magnitude of unit and each linear dimension of its configuration would increase by $\sqrt{3}$. In this octahedron the distances between the centre of octahedron and the centre of triangular faces would be $2\sqrt{3}$. The magnitude of the diagonal in the present case would be $4\sqrt{3} \times \sqrt{3}$.

The co-ordinates start from the centre of the octahedron and emanates in 4 radial directions towards 4

centres of triangular faces. In the 4 triangular pyramidal co-ordinates OABM, OADM, ODCM, OBCM or OABM', OADM', ODCM', OBCM' will operate on either side of ABCD. The volume of each triangular pyramidal quadrant from the centre is $4 \times 3 \times 3$ and for 4 quadrants on either side of the square ABCD it is $16 \times 3 \times 3$ which can be expressed as $(2\sqrt{3})^4$ in conformity with the configurations for the 1, 2, 3 dimensional co-ordinates as explained before. The 4 directions in this particular case would be emanating from the centre of the octahedron i.e. centre of the square ABCD towards either upward or downward as shown in fig. 25.



X=Centres of Triangular Faces
O=Centre of Octahedron
Fig. 25

CHAPTER 5

Square Continuum and Quantum Phenomena: Algebraic Representation

"One can give reasons why reality cannot at all be represented by a continuous field. From the quantum phenomena it appears to follow with certainty that a finite system of finite energy can be completely described by a finite set of numbers (quantum numbers). This does not seem to be in accordance with a continuum theory, and must lead to an attempt to find a purely algebraic theory for the description of reality. But no body knows how to obtain the basis of such a theory."

—Albert Einstein

This realisation of the necessity of an algebraic theory which could describe the reality satisfying mechanism of evolution both in terms of finite set of numbers as quantum numbers as well as simultaneously also satisfying the evolution in conformity with development of magnitudes of configuration representing reality in objective form in unified continuum incorporating the concept of variations in inertial co-ordinates from a previous to next in succession maintaining continuity would be fully justified from the discussions in general in the various works on the theory of universal wave including the present work and particularly in sections which follow.

(1) Significance of Universal Wave in Terms of Numerical Magnitudes of Squares in Continuum of Identical Square Units in a Plane

The increasing magnitudes of squares in a plane continuum of identical units have been discussed in a previous section where it was explained that the criteria which determine the progressive increase of magnitude of squares in sequence in one direction in a continuum of identical square units could be expressed symbolically as:

$+$, $-$, $\times$ and $\div$

The magnitudes in one direction are $1^2, 2^2, 3^2, 4^2, \dots$ and in 4 directions— $4 (1^2, 2^2, 3^2, 4^2, \dots)$. Figuratively, these are presented in fig. 26 (a) and (b) in plane continuum of squares.

Deductions which were made in the above approach for unidirectional development could also be made for development simultaneously in 4 directions. For example, in square continuum of identical units the following

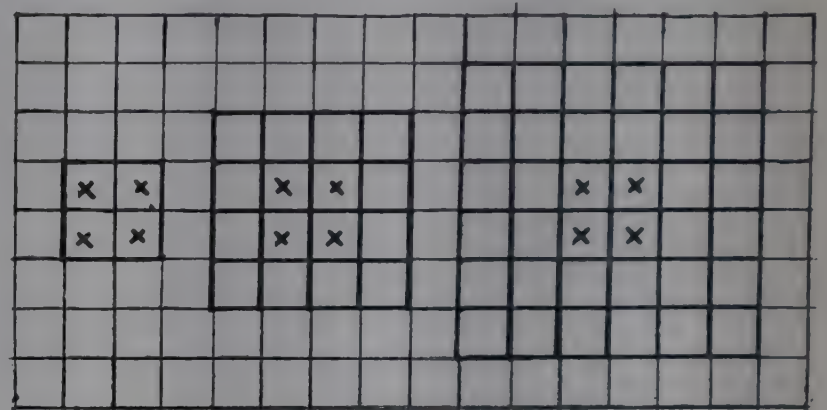


Fig. 26(a)—Continuum of Squares in Four Directions



Fig. 26(b)—Continuum of Squares in One Direction

criteria could be adopted for application to 4 directions.

0	1	2	3
0+0	1+1	2+2	3+3
0 =0	1 =4	2 =8	3 =12
0 ² +0 ²	1 ² +1 ²	2 ² +2 ²	3 ² +3 ²
+ +	+ +	+ +	+ +
0 ² +0 ²	1 ² +1 ²	2 ² +2 ²	3 ² +3 ²
=0	=4	=16	=36
0/0=1	1/1=1	2/2=1	3/3=1
Sum	1,	9,	25,
total			49

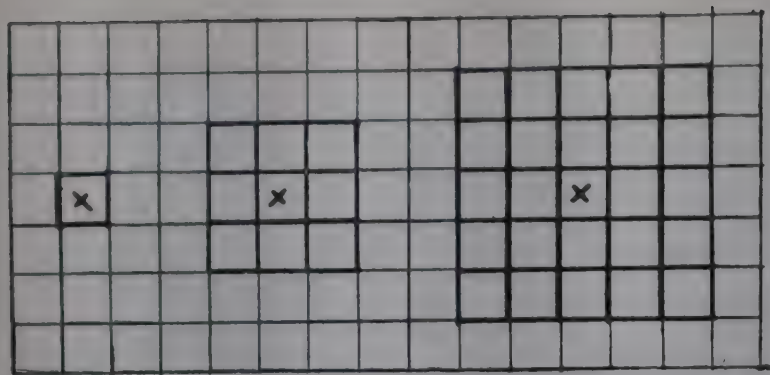


Fig. 27

The increasing magnitudes in this approach in the continuum would be $1^2, 3^2, 5^2, 7^2, \dots$

Figuratively, this is presented in fig. 27 in a plane continuum of identical squares.

The sequential development of square magnitudes in 4 directions in odd series as $1^2, 3^2, 5^2, 7^2, \dots$ is significant as against the previous even series $2^2, 4^2, 6^2, 8^2, \dots$, which was also the development of squares in 4 directions in increasing order of magnitudes in plane. These are the only simplest modes that are possible in the development of increasing magnitudes of perfect squares in plane continuum of identical square units.

From this, one comes to the conclusion that development of squares of increasing magnitudes in number in a continuum of plane has two modes. One mode follows the general formulae,

$$4. \frac{X}{Y}(1+2Y+Y^2)=4. \frac{X}{Y}(1+Y)^2;$$

the factor X/Y is actually the relativity co-efficients. If the square units which make up the continuum are identical then $X/Y=1$. The increasing magnitudes of squares in this continuum are 4 ($1^2, 2^2, 3^2, 4^2, \dots$) in 4 directions in plane. This is figuratively shown in figure 26(a) in which in the square configurations the 3 aspects viz. 1, $2Y$, and Y^2 are obvious. It may be remembered that these three aspects refer to 3 phases in the configuration of unit universal wave: superintensified, depleted and condensed respectively. In 4 directions in this mode, the algebraic general formula would be $(2X+0)^2$ in which X can have the values 0, 1, 2, 3, 4,

The other mode of development of square magnitudes

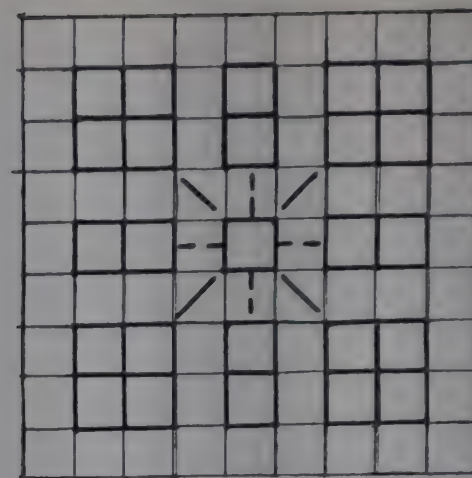


Fig. 28

in 4 directions as $1^2, 3^2, 5^2, 7^2, \dots$ also arise out of the distribution of the tetrahedra of unit magnitude in the unit universal wave in different phases. Here, in this mode the generalised formula for distribution arises out of the relationship as $5^2=4^2+3^2$. The general algebraic formula for this configuration is $(2x+1)^2$ in which X can have magnitudes as 0, 1, 2, 3, resulting in the series $1^2, 3^2, 5^2, \dots$. The break up of details pertaining to the 3 phases in the unit universal wave would be as: (fig. 28)

$$1+8+16 \text{ i.e. } (3^2+4^2)=25$$

$$\text{or } 1+4(1+1)+4(1+1)^2$$

This is reconciled with corresponding magnitudes as obtained for the different phases and zones in the configuration of the unit universal wave of regular tetrahedral configuration in fig. 29

The formula for distribution of tetrahedral units in this particular case is $1+4x+4x^2$ or $(1+2x)^2$. The digit 1 represents the central tetrahedron of the homogeneous zone. The digit 8 is for number of unit tetrahedra which are unrealised and correspond to the *depleted phase* of the heterogeneous zone of the wave and the number 16 for the 16 realized units of tetrahedron in the heterogeneous zone representing *condensed phase* of the wave.

If $(1+8+16)$ which is (3^2+4^2) i.e. 5^2 remain as unit which represents unit wave, then—

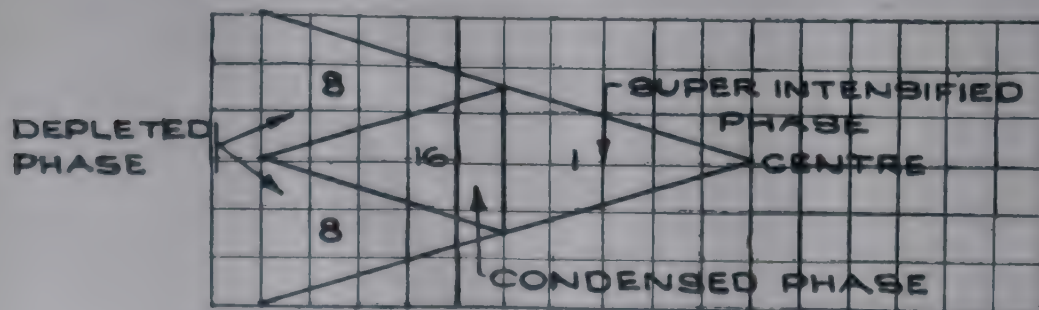


Fig. 29—Figurative Presentation of Configuration of Unit Wave Condensed to One Direction

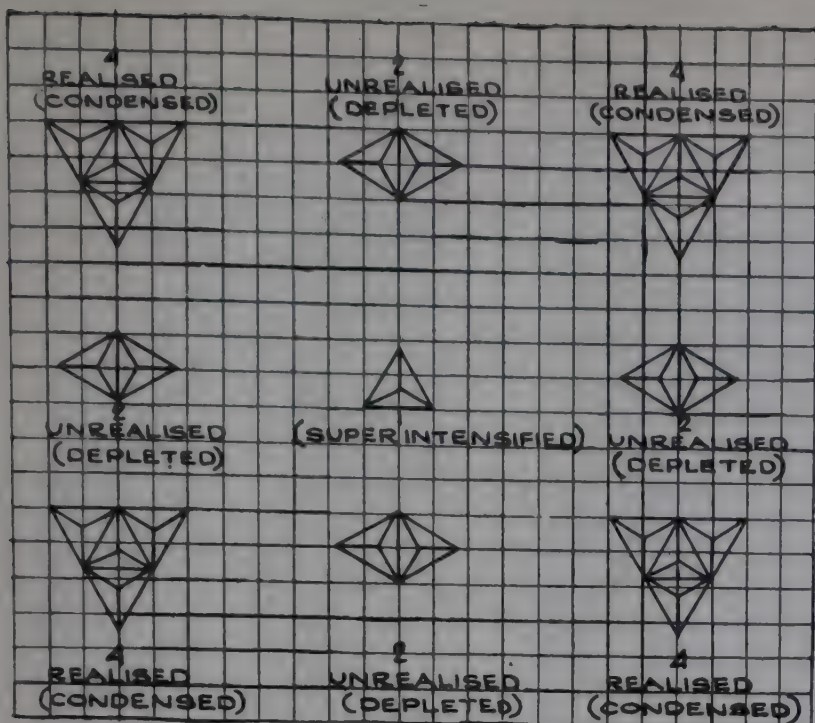


Fig. 30—Complete Unit Universal Wave of 25 Tetrahedra

(a) magnitudes of square units increase in 4 directions in plane as:

$$5^2, (1)^2, 5^2, (3)^2, 5^2, (5)^2, 5^2, (7)^2, \dots$$

Applying the general formula as:

$$1.5^2 + 4x.5^2 + 4x^2.5^2 \text{ and}$$

putting $x=0, 1, 2, 3, \dots$

the series becomes:

$$1.5^2, 9.5^2, 25.5^2, 49.5^2, \dots$$

or $5^2 (1^2, 3^2, 5^2, 7^2, \dots)$

5^2 retains constant magnitude as unit. (fig. 32)

(b) The Second mode is:

magnitude increases as:

$$5^2.1^2, 5^2.2^2, 5^2.3^2, \dots \text{in one direction in plane.}$$

In this magnitude of squares increase as 25, 100, 225, 400 in one direction or $5^2, 10^2, 15^2$ in one direction.

[fig. 33(d)]

And in 4 directions 4 ($5^2.1^2, 5^2.2^2, 5^2.3^2, \dots$)

which is 100, 400, 900....i.e. $5^2 (2^2, 4^2, 6^2, 8^2, \dots)$ or $10^2, 20^2, 30^2, 40^2, \dots$ [fig. 33(a)]

We thus have to discern the nature of evolutions in the two modes:

$$1^2, 3^2, 5^2, 7^2, \dots$$

$$0, 2^2, 4^2, 6^2, 8^2, \dots$$

Both modes give perfect square evolution in sequences of higher magnitudes in 4 directions in a plane.

The first case starts with one ready made square from which subsequently the magnitudes develop progressively in 4 directions.

$$\text{where, } x=0 \quad (2x+1)^2 = 1^2$$

$$1 \quad 3^2$$

$$2 \quad 5^2$$

$$3 \quad 7^2$$

The second case starts with point of position only

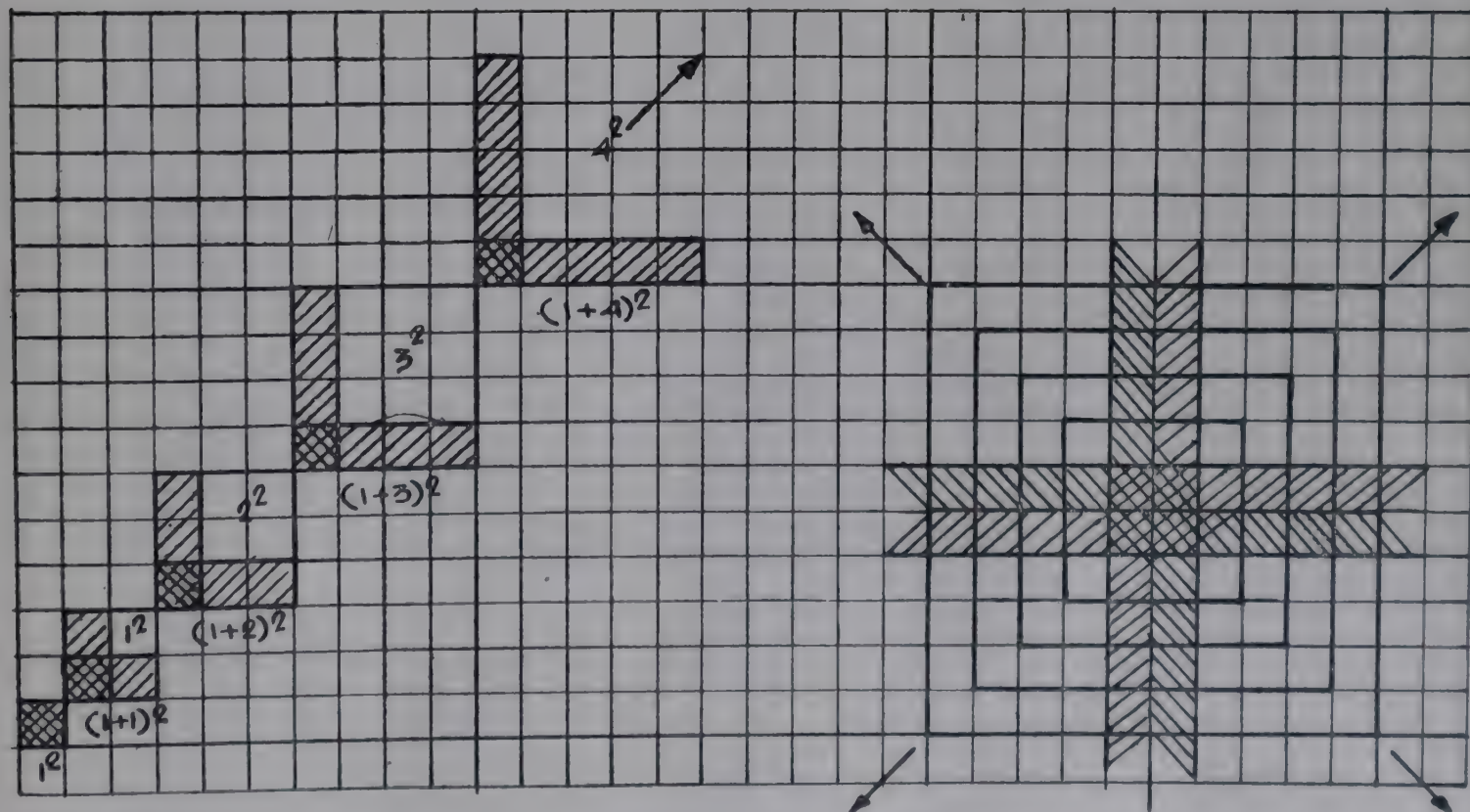


Fig. 31(a)—Continuum in One Direction
 $(1+2x+x^2)=(1+x)^2$

Fig. 31(b)—Continuum in Four Directions
 $4(1+2x+x^2)=4(1+x)^2$

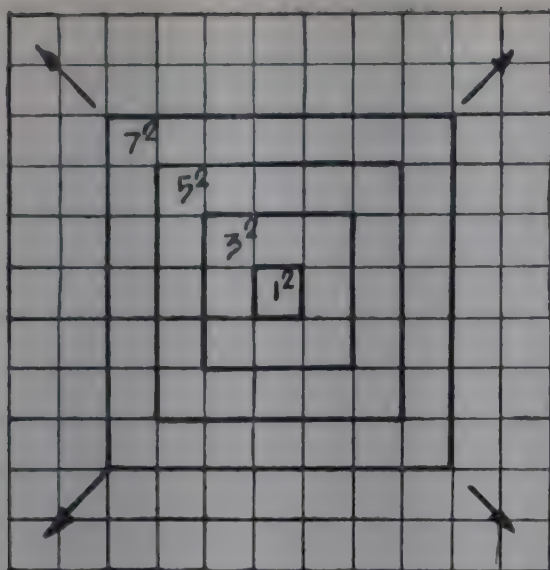


Fig. 32

(not square) from which the magnitudes of squares develop in sequence in increasing order in 4 directions in plane as $0^2, 2^2, 4^2, 6^2, 8^2, \dots$

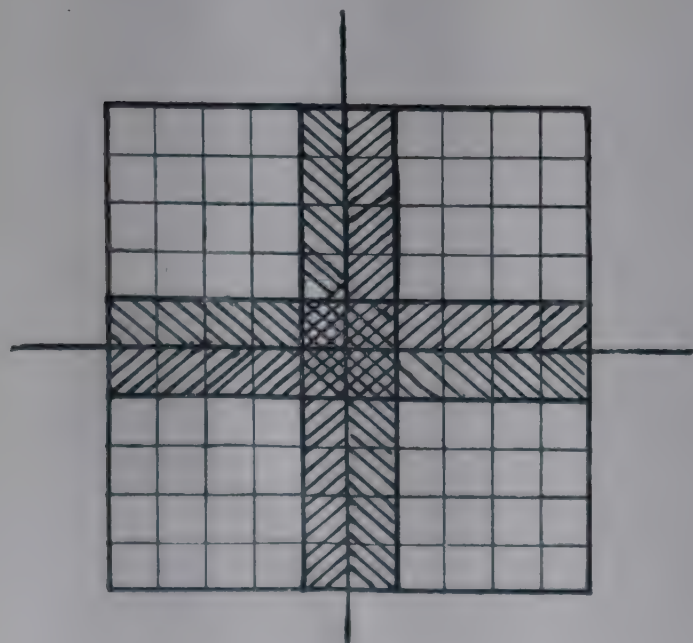
where, $x=0$ $(2x+0)^2 = 0^2$

1	2^2
2	4^2
3	6^2
4	8^2

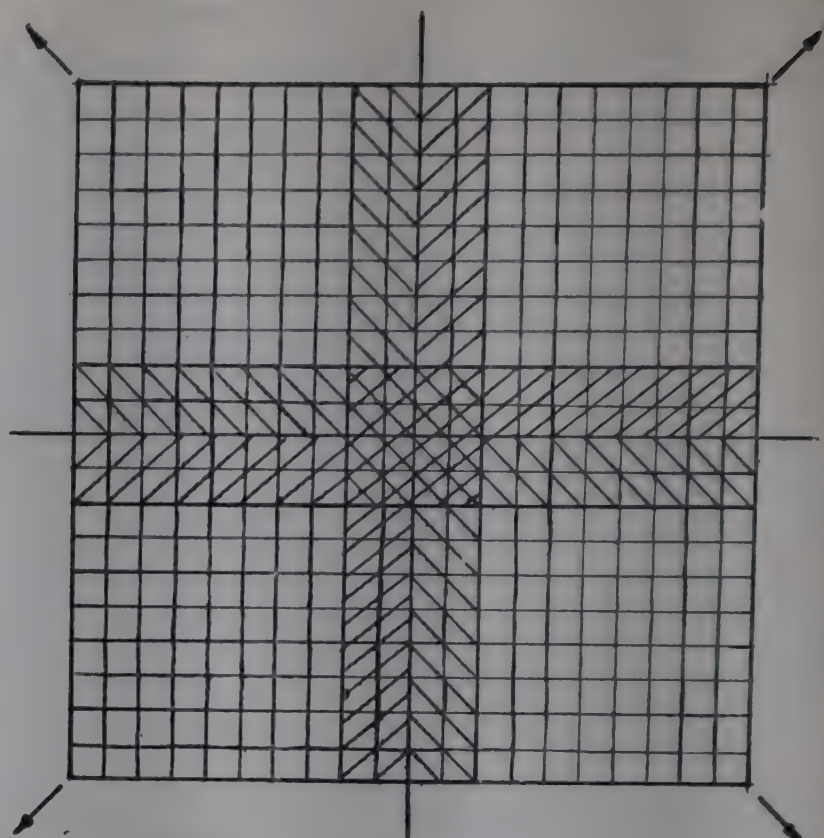
It may be noted that in fig. 31(a) the magnitudes of squares develop as $1^2, 2^2, 3^2, \dots$ in one direction only and in fig. 32 as $1^2, 3^2, 5^2, \dots$ in 4 directions.

From figs. 33(a), (b), (c) and (d) it may be discerned that in these the units are also changing in magnitudes along with the developing magnitudes of squares in the continuum.

Thus in fig. 33(a) the unit is 4.1^2 , in fig. 33(b) the



$(5^2.1^2)^4$
Fig. 33(a)



$(5^2.2^2)^4$
Fig. 33(b)

unit is 4.2^2 , in fig. 33(c) the unit is 4.3^2 and so on.

Here 5^2 unit in the configuration of increasing magnitude of waves remains constant.

If in this evolution unit remained constant at 5^2 then increasing magnitudes of squares in the continuum would have been in 4 directions as $5^2(1^2, 3^2, 5^2, 7^2, \dots)$ as would be discerned from fig. 32

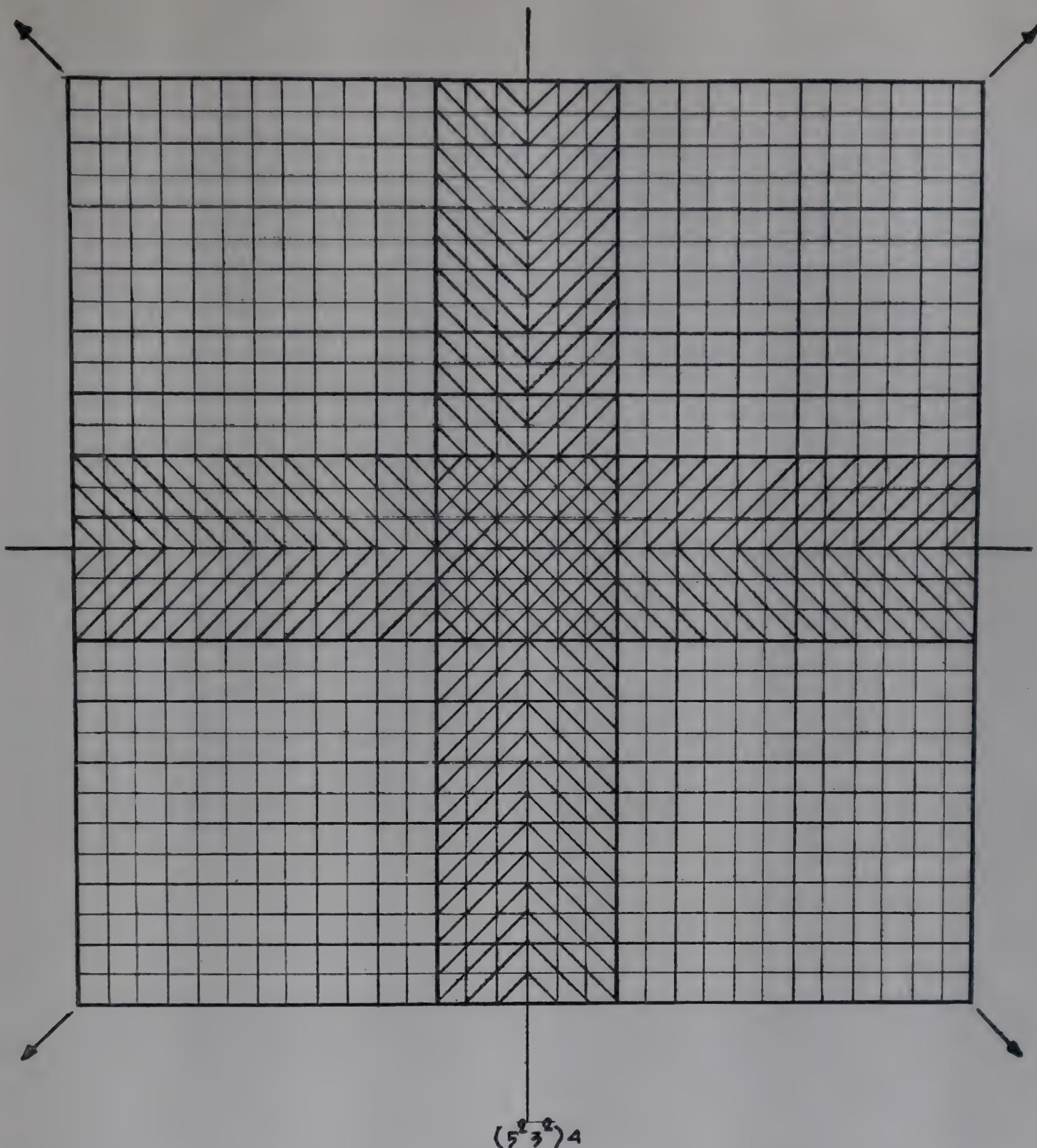
As against the above take figs. 33(a), (b), (c) in which unit remains constant as 4.1^2 but the magnitudes of evolved squares vary as $(1+x)^2$ [as $(1+0)^2, (1+1)^2, (1+2)^2, (1+3)^2, \dots$]

Further, the numbers 1, 8 and 16 sum total of which is 25, represent the three phases of the unit universal wave of tetrahedral configuration which is the most isotropic, and from which the square configuration in a plane has been derived, and from which the phases pertaining to 1 and 8 have been derived which are similar in nature except that 1 is superintensified and 8 is depleted. The 16 represents condensed phases. Therefore, $1+8$ represents one phase in continuity and 16 represents another segregated phase. Thus the equation $3^2+4^2=5^2$ when multiplied on both sides by any square would give a perfect square representing the corresponding magnitude of universal wave.

Thus, $(1+8)(x)^2=3^2(x)^2$

and $16(x)^2=4^2(x)^2$

Putting $x=0, 1, 2, 3$



$$(5^2 3^2) 4$$

Fig. 33(c)

Sum total in these also should give perfect squares:

$$\begin{array}{rcl} 3^2(x)^2 & = 0^2 & 4^2(x)^2 = 0^2 \\ & 3^2 & 4^2 \\ & 6^2 & 8^2 \\ & 9^2 & 12^2 \\ & 12^2 & 16^2 \end{array}$$

Sum total of the above two are:

$$\begin{array}{l} 0^2 + 0^2 = 0^2 \\ 3^2 + 4^2 = 5^2 \\ 6^2 + 8^2 = 10^2 \\ 9^2 + 12^2 = 15^2 \\ 12^2 + 16^2 = 20^2 \end{array}$$

In the two series $1^2, 3^2, 5^2, 7^2, \dots$ and $0^2, 2^2, 4^2, 6^2, \dots$ their sums as such are not perfect squares in any direction whereas in the present sum total of the two series in any state is a perfect square in one direction. Further, sum of two consecutive squares of 3 and 4 only makes perfect square on subsequent 5, i.e. $3^2 + 4^2 = 5^2$ and no others.

In 4 directions 2 multiplied by roots in the series required to be added.

$$\begin{array}{rclcl} \text{Thus} & 0^2 + 0^2 + 2.0.0 & = 0^2 & & \\ & 3^2 + 4^2 + 2.3.4 & = 7^2 & = (3+4)^2 & \\ & 6^2 + 8^2 + 2.6.8 & = 14^2 & = (6+8)^2 & \end{array}$$

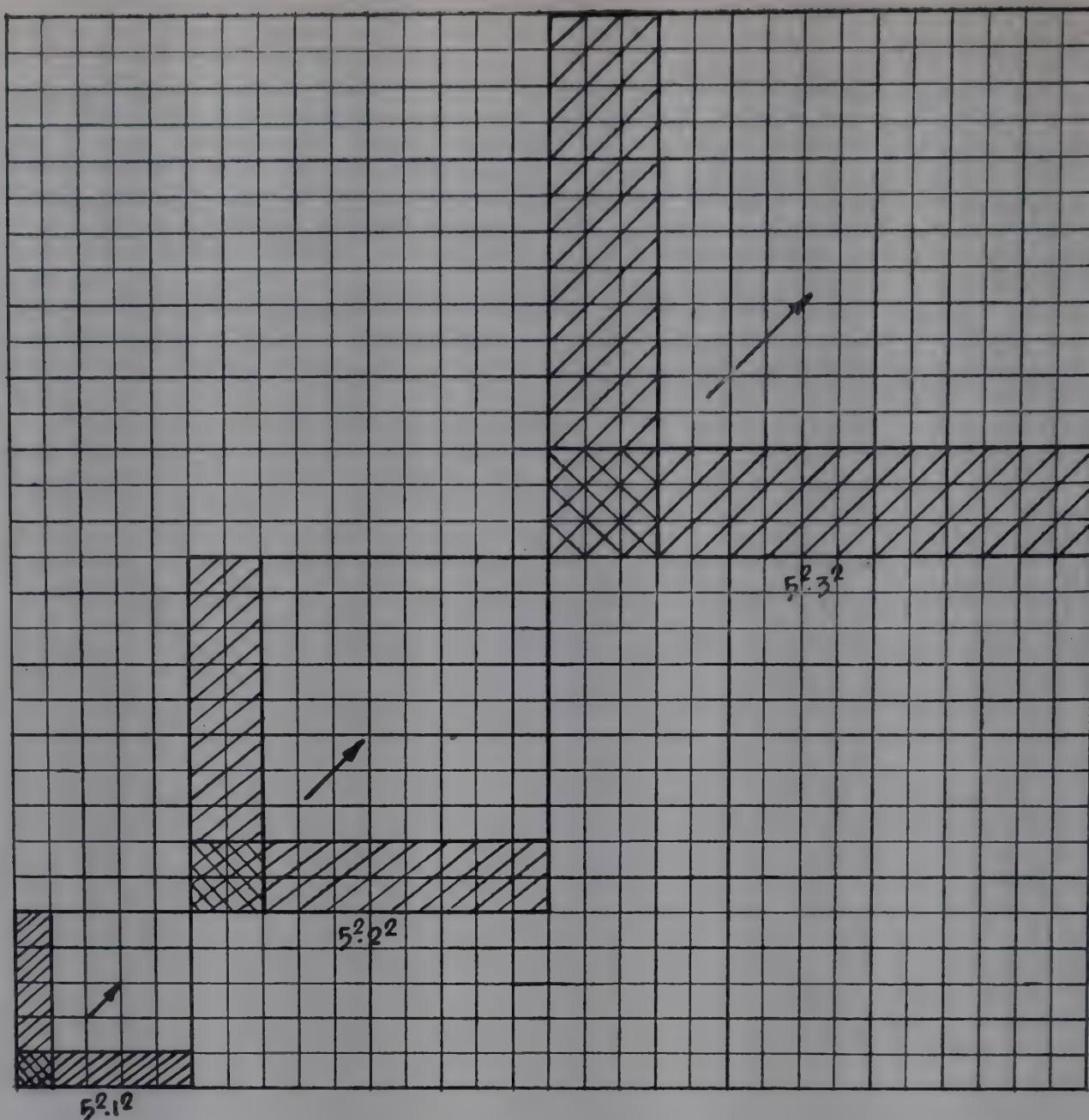


Fig. 33(d)

$$\begin{aligned} 9^2 + 12^2 + 2 \cdot 9 \cdot 12 &= 21^2 = (9 + 12)^2 \\ 12^2 + 16^2 + 2 \cdot 12 \cdot 16 &= 28^2 = (12 + 16)^2 \end{aligned}$$

Significance of π

$$\begin{aligned} &\frac{11}{7}, \quad \frac{25}{14}, \quad \frac{39}{21}, \quad \frac{53}{28} \\ &= \frac{11}{7}, \quad \frac{11+14}{14}, \quad \frac{11+2 \cdot 14}{21}, \\ &\quad \frac{11+3 \cdot 14}{28} \end{aligned}$$

In this continuum magnitudes of ratio of square units forming diagonal and square units forming orbits as products of a constant magnitude of unit ratio which is $22/7$.

(2) Continuum and Power of Dimensions of Co-ordinates

In previous sections attempts were made to describe

the concept of continuum of one, two, three and four dimensional cases. The quantitative descriptions of magnitudes however were solely guided by the concept of magnitude as digits and numbers which are derived from the relative magnitudes of dimensions in the con-

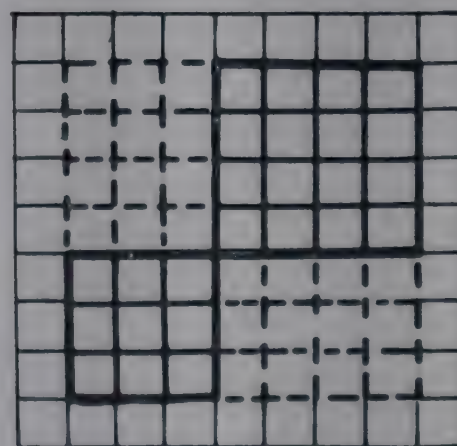


Fig. 34

figuration of square units making the continuum. The projected configuration of square in a plane is in turn derived from the configuration of regular tetrahedron itself. The linear, square and cubic continuum can be easily presented in their configuration by the relative magnitudes of dimensions that are involved in the configurations of squares. Difficulty arises in case of the four dimensional continuum for which an alternative description may be necessary. The magnitude of configuration of the linear, square and cubic continuum can be described with respect to the different relative magnitudes of reference co-ordinates in the configuration. For example, the magnitude of configurations of straight direction, square and cube can be represented by either in terms of their magnitude of extent of the straight line, or as area on the square of the sides, or as volume content of cube. The configurations can also be represented in terms of linear magnitudes as the extent of line for unidimensional coordinate, extent of diagonal for two directional square and the extent of diagonal for 3 directional configuration of cube. Symbolically in the first alternative these can be represented by

a^1, a^2, a^3, a^4 and in the second case they can be represented linearly as $a\sqrt{1}, a\sqrt{2}, a\sqrt{3}, a\sqrt{4}$ etc. (in this case reference may be made to fig. 12).

In the previous sections the two modes of developments of configurations involving different dimensional significance have been explained, assuming magnitude of unit of linear distance as $2\sqrt{3}$ which is the linear magnitude of side of square generated from projection of unit tetrahedron on a plane in the manner described before.

In the following an attempt will be made to describe the mechanism of development of the magnitudes and variation of magnitudes of dimensions not only within each reference frame of coordinates belonging to one, two, three or four dimensional continuum, but also to describe the mechanism of development of the magnitudes as powers of dimensions of coordinates increasing from one, two, three and four dimensional cases: i.e. when they increase from unidimensional to two dimensional, from two dimensional to three dimensional and from three dimensional to four dimensional and so on.

In the following instead of taking $2\sqrt{3}$ as the magnitude of unit of straight distance which was assumed in previous discussions, we shall assume the usual unit for magnitudes in one direction.

It would be recalled that one of the basic postulates in the theory of universal wave is that any concept whatever be its nature of manifestation must contain two opposite aspects and the sum total or resultant of the

two opposite aspects makes the equilibrium configuration of the concept or the manifestation. In order to explain completely a phenomenon it is therefore absolutely essential to not merely see and find out one aspect only, but also the other associated opposite also to be considered which makes it complete.

In the following illustration (+) and (−) signs associated with the magnitudes should not be taken in conventional sense such that for example $-3^3 + 3^3$ could be taken as one negative -3^3 and another $+3^3$, the sum total of which conventionally would be zero. This would not be the meaning of the signs (−) and (+) in the following illustrations. The (−) and (+) in the following would merely mean that the two are in opposite phases or opposite directions so that the association of (−) magnitude and the (+) magnitude together gives the sum total. Thus $-3^3 + 3^3$ would really mean the numerical magnitude of 2×3^3 . The real significance of (−) and (+) associated with the magnitudes will be explained further later where the real physical significance of (+) and (−) in square continuum will be shown and the physical meaning will be brought out by adopting the algebraical approach to this problem. In the following (Table 1) illustrations in (A) it has been shown how two opposite magnitudes having zero power would generate a unidimensional magnitude. In (B) similarly it has been shown how two opposite magnitudes having unit power, i.e. unidimensional magnitude, generate a two dimensional square magnitude. Similarly in (C), it has been shown how two opposite square magnitudes would generate a cubic or 3 dimensional magnitude. Similarly in (D), following the same lines, the generation of 4 dimensional magnitudes from 3 dimensional opposite magnitudes has been shown.

TABLE 1

A	$[(-1)^0 + (+1)^0] 1/2$	$= (1)^1$
	$[(-2)^0 + (+2)^0] 2/2$	$= (2)^1$
	$[(-3)^0 + (+3)^0] 3/2$	$= (3)^1$
B	$[(-1)^1 + (+1)^1] 1/2$	$= 1^2$
	$[(-2)^1 + (+2)^1] 2/2$	$= 2^2$
	$[(-3)^1 + (+3)^1] 3/2$	$= 3^2$
C	$[(-1)^2 + (+1)^2] 1/2$	$= 1^3$
	$[(-2)^2 + (+2)^2] 2/2$	$= 2^3$
	$[(-3)^2 + (+3)^2] 3/2$	$= 3^3$
	$[(-4)^2 + (+4)^2] 4/2$	$= 4^3$
D	$[(-1)^3 + (+1)^3] 1/2$	$= 1^4$
	$[(-2)^3 + (+2)^3] 2/2$	$= 2^4$
	$[(-3)^3 + (+3)^3] 3/2$	$= 3^4$
	$[(-4)^3 + (+4)^3] 4/2$	$= 4^4$

(3) Algebraic Formulae for the Two Opposite Modes in Square Evolution in Plane Continuum

The two opposite modes of square evolutions are viz. $1^2, 3^2, 5^2, \dots$ and $0^2, 2^2, 4^2, 6^2, \dots$

The algebraic formula representing the first mode of evolution is $(2X+1)^2$ representing $1^2, 3^2, 5^2, 7^2, 9^2, \dots$ and $(2X+0)^2$ representing $0^2, 2^2, 4^2, 6^2, 8^2, \dots$ the second mode. Their overall sum would give the so called continuous series as $0^2, 1^2, 2^2, 3^2, 4^2, \dots$

Strictly speaking, getting further into detail for the value of X which would represent negative as well as positive directions as well as those of 1 and 0 in the two algebraic formulae, the alternative algebraic formula for the first mode can be $[2(-X)+(-1)]^2$ and $[2(+X)+(+1)]^2$. The magnitudes of the evolved squares in these two alternatives would be—

$$\begin{array}{cccc} (-1)^2, & (-3)^2, & (-5)^2, & (-7)^2 \\ \text{and } (+1)^2, & (+3)^2, & (+5)^2, & (+7)^2 \end{array}$$

The figurative presentation on plane square continuum of these indicating the significance of $(-)^2$ and $(+)^2$ is explained in figs. 35 & 36.

The relative directions of development of magnitude of squares in opposite nature would be clearly seen from figure 35; though $(-1)^2$ is conventionally equal to 1^2 or $(+1)^2$ is equal to also 1^2 , but when the development of magnitudes of squares incorporates both negative and positive directions relative to a ground state, the relative difference in spatial significance (space-time-continuum) of $(-1)^2$ and $(+1)^2$ would be obvious. The two squares may be of identical magnitude,

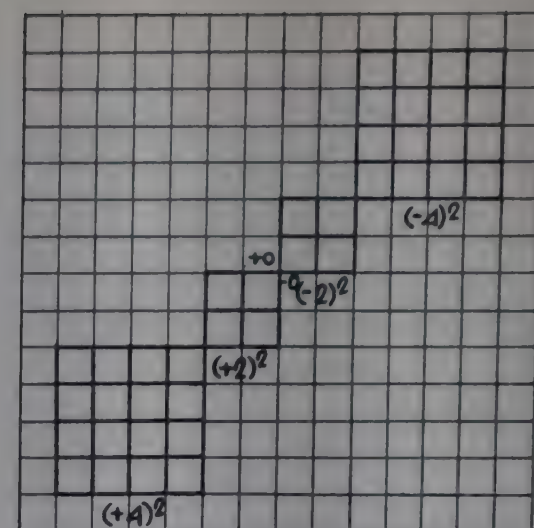


Fig. 36

but they are opposite in space time orientation.

Similarly for the second mode, the algebraic formula incorporating the positive and negative aspects would be

$$[2(-X)-0]^2 \text{ and } [2(+X)+0]^2$$

Incorporating the value of X in these, the two magnitudes in the positive and negative directions would be as follows:

$$\begin{array}{cccc} (-0)^2 & (-2)^2 & (-4)^2 & (-6)^2 \\ (+0)^2 & (+2)^2 & (+4)^2 & (+6)^2 \end{array}$$

The figurative presentation may be seen in fig. 36.

In this case also the difference in significance between the square of $(-)$ magnitude and the square of $(+)$ magnitude can be realised in their opposite orientation in space time continuum.

The algebraic formula for the continuum of square evolution can be represented in the two modes in the above by

$$[2(-X)+(-1)]^2 \text{ and } [2(+X)+(+1)]^2 \text{ for the first mode.}$$

And $[2(-X)-0]^2$ and $[2(+X)+0]^2$ for the second mode.

and they would represent the evolution involving 4 directions in the square (plane) continuum.

The increase of magnitude of squares in plane square continuum in one direction however would be represented by the following algebraic formula incorporating both $(+)$ and $(-)$ aspects:

$$[1(-X)+(-1)]^2 \text{ and } [1(+X)+(+1)]^2$$

as well as

$$[1(-X)-0]^2 \text{ and } [1(+X)+0]^2$$

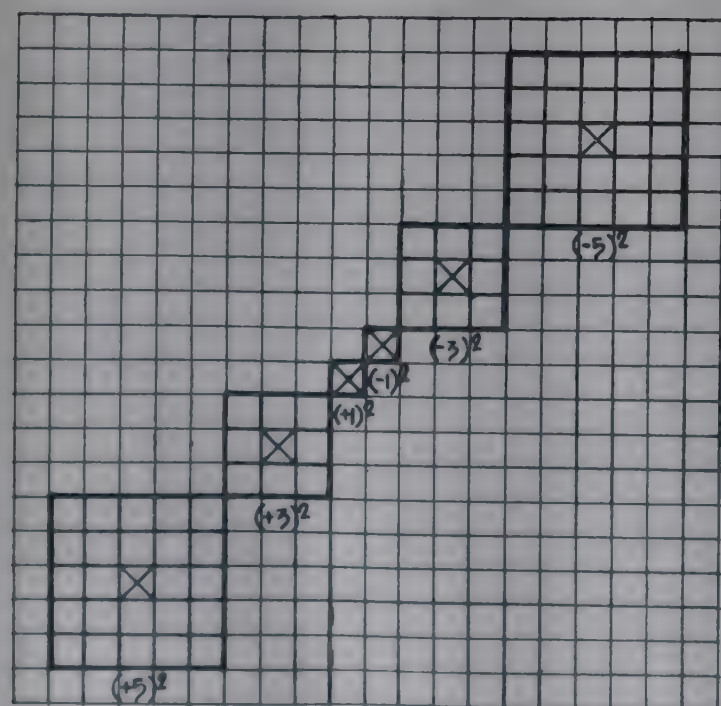


Fig. 35

In the first alternative, the increasing magnitudes of squares would be with $X=0, 1, 2, 3, 4, \dots$

as $(-1)^2 \quad (-2)^2 \quad (-3)^2 \quad (-4)^2 \quad \dots$
and $(+1)^2 \quad (+2)^2 \quad (+3)^2 \quad (+4)^2 \quad \dots$

In the other case the magnitude of squares would be

$(-0)^2 \quad (-1)^2 \quad (-2)^2 \quad (-3)^2 \quad (-4)^2$
 $(+0)^2 \quad (+1)^2 \quad (+2)^2 \quad (+3)^2 \quad (+4)^2$

The significance of opposite nature of orientation in direction in this case also would be similar to figs. 35 and 36 as shown in fig. 37.

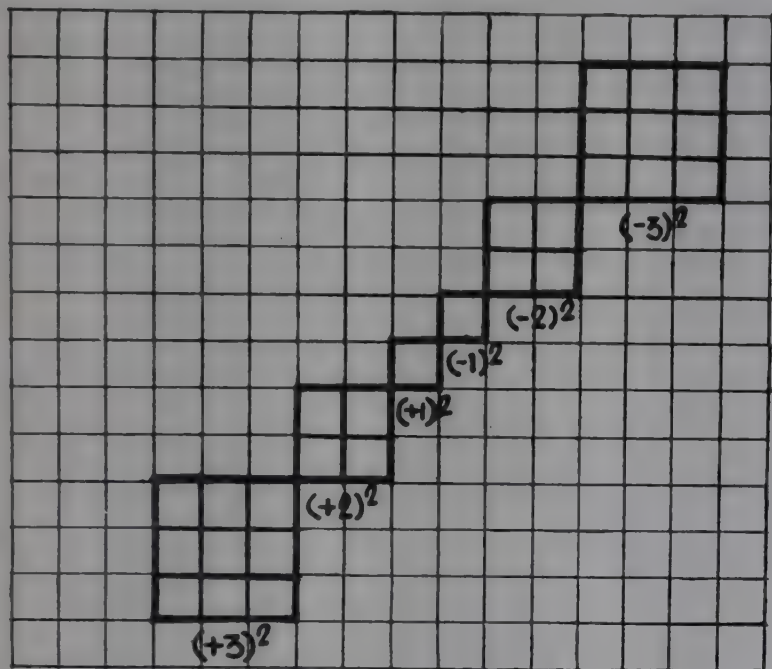


Fig. 37

These opposite modes in square evolution in four directions are represented by algebraic formula as below:

For one mode $[2(\mp X) + (\mp 1)]^2$ representing $1^2, 3^2, 5^2, \dots$ and for another mode $[2(\mp X) + (0)]^2$ representing $0^2, 2^2, 4^2, 6^2, \dots$ and the corresponding orientation of the square configuration in opposite sense which has been shown in figs. 35 and 36 respectively will throw light in the mechanism of development of cubes from square configuration. The development of progressive increase of powers of magnitudes from a previous to subsequent has been indicated before in table 1. Apparently, though in a very elementary way the development of magnitudes from lower to higher powers of increasing order has been shown in table-9, and previous to that in fig. 12, still their real physical significance might not be clear from mere perusal of the table 1 and fig. 12; but when table 1 would be examined along with the significance derived from the algebraic formulae of square evolution incorporating the positive and negative aspects and opposite modes in their orienta-

tion as shown in figs. 35 and 36, the mechanism of development of the magnitude representing the configuration from a lower to higher power would be revealed.

For example, take the case of development of cubic continuum or configuration from square configuration. The square configuration following say $1^2, 3^2, 5^2, \dots$ mode from fig. 35, has opposite pairs of squares having opposite orientation as $(-1)^2$ and $(+1)^2$, $(-3)^2$ and $(+3)^2$, $(-5)^2$ and $(+5)^2, \dots$

The magnitude of the coordinate linking these two opposite square units is the sum of $(+\frac{1}{2})$ and $(-\frac{1}{2})$, of linear unit as would be obvious from fig. 38(a) which would explain the development of unit cube.

Similarly $(-3)^2$ and $(+3)^2$ in their opposite orientation when coordinated by sum of $(-\frac{3}{2})$ and $(+\frac{3}{2})$, as shown in fig. 38(b) with corresponding implications therein, will show the generation of 3^3 and so on and so forth. Applying fig. 36, similarly, the generation of the even cubes from the corresponding squares of even magnitudes would also be clear.

Generalised formula for development of power of continuum is:

$$[(+X)^i \text{ plus } (-X)^i] X/2 = X^{i+1}$$

In this, i represents index or power of dimensions of co-ordinates for a continuum of one inertial reference frame of co-ordinates whose power is i . For different reference frames of co-ordinates (i.e. different dimensional systems) values of i would be different, which would be 0 for invariant co-ordinate system, 1 for unidimensional system, 2 for two dimensional system, 3 and 4 for three and four dimensional systems respectively.

Within any one reference frame of coordinates of constant value of i , magnitude of X can vary.

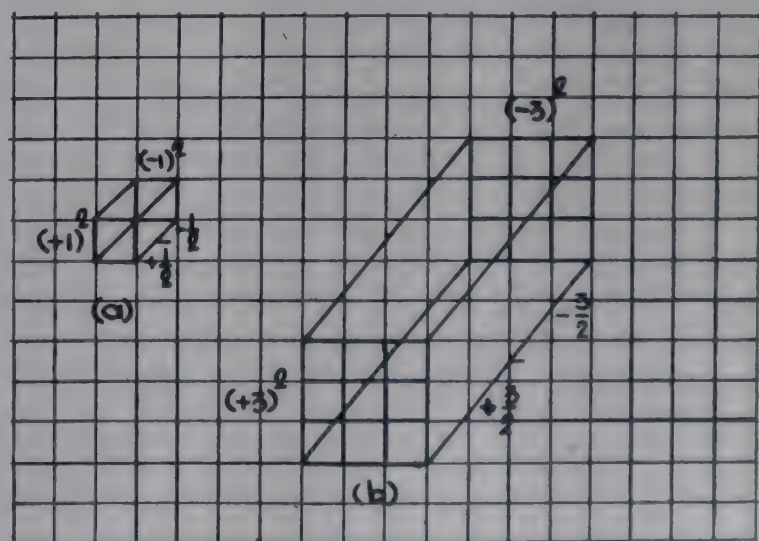


Fig. 38

Thus variation of X in an invariant system in the above formulae, where $i=0$ and X would be 1, 2, 3.... would give unidimensional magnitudes of X, as $1^1, 2^1, 3^1...$ as deduced in A in table 1.

Similarly variation of X in unidimensional (uni-variant) system where $i=1$, $X=1, 2, 3....$ would give two dimensional magnitudes of X, as $1^2, 2^2, 3^2....$ as derived in B in Table 1.

Again, variation of magnitudes of X in two dimensional (bi-variant) system where $i=2$, and $X=1, 2, 3....$ would give the three dimensional magnitudes of X as $1^3, 2^3, 3^3....$ as shown in C in Table 1.

And variation of X in three dimensional (trivariant) system where $i=3$, and $X=1, 2, 3....$ would give the four dimensional magnitudes of X as $1^4, 2^4, 3^4....$ as shown in D in Table 1.

The above illustration explains the mechanism of change of magnitude of a dimension X within one inertial reference frame of co-ordinates of constant power of i on the one hand and also change of magnitudes of power of reference frames of co-ordinates from one to next of higher magnitude on the other.

From the above, a conclusion of great consequence can now be enunciated:

While in one inertial reference frame of co-ordinate system (frame) of constant power, magnitudes may vary in terms of their constant power, powers of co-ordinates vary from one frame to another of next higher magnitude as resultant of variation in opposite phases in a frame of co-ordinate of lower power following the general formula.

$$[(+X)^i + (-X)^i] X/2 = X^{i+1}$$

This explains the significance of reference frame of co-ordinate of constant power (in so called inertial frame or constant gradient) on the one hand and different frames of coordinates of varying power (multidimensional variations) in a continuum of non-inertial co-ordinates on the other.

Significance of gradient variations in continuum involving constant gradient like constant power is one case, the other case is unified continuum of varying magnitudes of gradients like varying magnitudes of powers. This will be explained further in fig. 40 (a) and (b).

(4) Magnitude: its two aspects

One of the basic premises of the theory of universal wave is the important law of nature in the context of finite phenomenal universe which states—"perception is

always less than what it was in conception". The same also can be expressed in another way in terms of abstract and concrete. Abstractness is not defined by any limits or bounded by any objective configuration etc. But when that abstract concept is rendered concrete or objective by association with certain cognisable configuration, the abstract takes a concrete form as objective and becomes perceptible to senses. The terms conception and abstractness appear to be similar in their significances. Since conception about certain aspect is defined in imagination and thoughts which has really no limiting configuration while it remains as a concept. But when that aspect takes a concrete form by being translated into some shape or form rendering that amenable to perception through physical senses, it becomes limited in its degree of freedom. We have given examples to explain this with illustrations of football and moon in one of the works* by the author.

Suppose a three dimensional picture like that of a tree is viewed through a telescope and taken a photographic picture on plane of paper. The three dimensional concept has been translated into a configuration in two dimensional plane. The former had certain degrees of freedom, but when translated into configuration in a plane it has lost some degree of freedom.

The similarity of realisation by physical perception of a concept is equivalent in its significance when one would apply the principle to realisation of a spacial configuration through apparatus (inanimate as well as animate). The magnitude of objective realisation of such a concept of configuration would depend on many factors. We have cited only very simple cases like attempting to realise the nature and magnitude of a natural phenomenon through photographic means in a plane of paper or projecting a configuration or trying to define the magnitude of perception of an object at varying distances as in the case of the illustration of football and moon moving in its orbit. When a football is too near it cannot be perceived, when it is too far also it is not perceptible, and when it is at optimum distance of perception, then only maximum of 50% of the actual configuration of the football is perceived.

It is relevant to mention about deductions in the different Darshanas—Vaisheshik, Nyaya and Sankhyya Darshanas. The magnitude of physical realisation of a concept in perception would depend on various factors as is mentioned in Sloka VII of Sankhyyakarika:

* Energy Field of the Universe and Atom—Part II, *Technol.* 2 (4) (1965) (Chapter I)

The magnitude of perception of a real thing would be less from the following criteria:

Too far,

Too near,

Defects in perceiving apparatus,

The intensity of power of observation of the observer,
Defect in the physical organ,

Extreme subtlety of the object—too subtleness of the thing to be perceived,

Obstacles in the path of realisation or perception,
(Say property of a medium through which observation is carried out),

Confusion about the thing being mixed up with similar or other things.

Though the factors affecting the correct perception of magnitude, indicated in the sloka, comprise of both animate and inanimate aspects, but one cannot deny that in the direction of correct realisation of a thing, whatever it be, whether it is a configuration or any phenomenon or an event that takes place, all these factors are involved. However, it is not intended to discuss the contributions of the different Darshanas and their achievements, which are well known, the exactness and accuracy of which would be obvious since these form the very basis of evolution of numbers and digits, decimal systems which have been developed by applying those concepts and subsequently the various mathematical operations. The purpose of mentioning this here is to bring out the fact that the concept of magnitude has two significant aspects, namely, the quantitative and intensive aspects.

Regular Tetrahedron and Square

A regular tetrahedron when projected on a plane with any pair of opposite sides parallel to the plane surface; the projected configuration of tetrahedron on plane is a square. The two-dimensional projected square has less number of coordinates than the configuration of the regular tetrahedron. Instead of configuration of tetrahedron and its projected configuration of square on plane, one can consider in terms of configurations with multi-co-ordinate system. For example a three dimensional cube can be projected on a plane as square. It can also be projected as other two-dimensional configurations on plane. It is also possible to visualise a cube such that it can be represented by its diagonal as unidimensional straight magnitude. A square configuration in a plane can similarly be described by linear magnitude by its diagonal in the same plane. This aspect

has been discussed with figs. 20, 21 and 22; wherein the linear magnitude $2\sqrt{3}$ was not just an arbitrary choice but it is the magnitude of the side of the projected square on plane from a regular tetrahedron whose distance between the centre and the centre of any triangular face is 1. In order to retain the link of the resulting configurations like line, square, cube, octahedron etc. with the original regular tetrahedron from which these configurations have been generated, the linear magnitude of $2\sqrt{3}$ was used as the basis for the resulting unidimensional, two-dimensional, three-dimensional and four dimensional configurations as $(2\sqrt{3})^1$, $(2\sqrt{3})^2$, $(2\sqrt{3})^3$, $(2\sqrt{3})^4$.

Now if those very configurations were to be realised or perceived in a plane by straight linear unidimensional magnitudes, say, by diagonals of their configurations, then those magnitudes would be $(2\sqrt{3} \times \sqrt{1})$, $(2\sqrt{3} \times \sqrt{2})$, $(2\sqrt{3} \times \sqrt{3})$... respectively. What is wanted to be conveyed here is that in order to realise quantitatively a multi-dimensional concept of configuration or continuum by projecting to one of less number of co-ordinates, the projected configuration will have less degree of freedom or will possess less number of co-ordinates describing the projected configuration relative to the original multi-dimensional concept of configuration. In other words, the inertial configuration having certain number of co-ordinate systems when admitted to be analysed or perceived or realised on a certain concrete platform like a plane (that is a configuration having less number of co-ordinates than the original) through limited means, the magnitude of configuration and the co-ordinates of the translated or projected one does not remain the same in its magnitude or in its co-ordinate as those of the original configuration.

In the above example $(2\sqrt{3})^1$, $(2\sqrt{3})^2$, $(2\sqrt{3})^3$ etc. and their linear presentation as their diagonal as $2\sqrt{3} \cdot \sqrt{1}$, $2\sqrt{3} \times \sqrt{2}$, $2\sqrt{3} \times \sqrt{3}$, $2\sqrt{3} \times \sqrt{4}$... respectively is the linear projection from unidimensional, two-dimensional, three-dimensional... magnitudes.

There can be another mode of projection also. For example, we can take the expression of increasing magnitude of numbers of identical square units in terms of linear magnitudes as has been explained with the help of fig. 12.

In the discussion on fig. 12 it has been shown that when a linear magnitude increases in such a manner that the squares on those are equal to multiples of certain square units by increasing magnitude of numbers, then those linear magnitudes can be expressed in terms of square units as one square unit as 1.1^2 , two square units as 2.1^2 , three square units as 3.1^2 ... But if those will be

expressed in terms of linear magnitudes then they will be expressed as linear unit multiplied by the roots of magnitudes of the numbers as $1 \times \sqrt{1}$, $1 \times \sqrt{2}$, $1 \times \sqrt{3}$... The significance of these two observations will be dealt with further later but in the present context we were trying to explain that like the conception and perception or abstract and concrete etc. magnitude also had two aspects. Magnitude may relate to something, some dimension like conception or abstractness on the one hand, the other aspect of magnitude may relate to objective or concrete or perceptible or quantitative or concrete in certain shape or form which is amenable to perception to human senses on the other.

These aspects of magnitude have been the subject matter of discussion through millenia. But the exact definitions of the two aspects when applied to specific manifestation in the phenomenal world has not become completely clear. This is because any phenomenon in the world has got two aspects. An aspect which is amenable to our senses, call that by whatever name—perception, concrete, objective, certain, definite, distinguishable, definable etc. on the one hand and abstract, conception, uncertain, unknown, indistinguishable, indefinite, undefinable etc. on the other. Main problem is to analyse each and every specific problem and classify the results pertaining to these two opposite aspects and establish relationships in terms of magnitude for all those in each category on the one hand and between the two or more categories on the other.

Suppose by common symbol of digits and numbers quantitative ideas may be conveyed by 1, 2, 3, 4, 5, 6... of a certain category. But the other aspect which is the abstract aspect, which conveys the status of category, as first category, second category, third category etc....; magnitudes of that also require to be understood and incorporated. The quantitative aspect of magnitude can be extensive aspect and the status aspect of magnitude can be intensive aspect like intensity or potential. The latter can be also termed as status, levels and such other terms which convey the significance. The two terms quantity, and quality also would convey the significances of the two aspects of magnitude.

(5) Variation of Magnitudes in Continuum: Inertial and Non-inertial

Einstein's continuum involving inertial co-ordinates and continuum involving non-inertial co-ordinate also would convey the nature and variation of magnitudes in

two different manners as similar to the two significant aspects of magnitude as explained in the above. Similarly the variation of magnitude of a property of thermodynamic phases also would convey the two different cases of variation—the variation in magnitude of property in continuum in a single phase, i.e. continuum retaining the phase constancy; the other is change of magnitudes of property which may vary from one phase to another phase in sequence, i.e. variation of the magnitude of property in continuum involving different phases. A single phase can be a concept of continuum of inertial co-ordinate system for variation of magnitude of a property of the constituent of the phase. This is one aspect. The other aspect is the continuum involving different phases having different inertial co-ordinates through which change occurs and would convey the other nature of variation of magnitude of property of the constituents in the different phases relative to certain state in each continuum, which would bring in the aspect of intensity or relativity.

If there are several rows of books and each row having a number of identical books and the books in different rows are different from previous, then the variation of magnitude of number of identical books in each row conveys one aspect of magnitude. But if there could be a relationship between the books in the first row with second, second with third, third with fourth and so on, then the continuum of the change of magnitudes involving all the rows in serial order of magnitude of status, viz. first level, second level, third level, or first row, second row, third row, etc. will convey the other aspect of magnitude.

Roots of Squares and Roots of Number of Square Units

In the discussions on fig. 12 it was explained that the radials a, b, c, d, e, linear magnitudes of which were the root of the sum of numbers of the square units on a constant side and the other on progressively varying in magnitude as numbers of squares units as 1 square unit, 2 square unit, 3 square unit... or $1.a^2$, $2.a^2$, $3.a^2$ and so on. The increasing magnitudes of a, b, c, d...etc. may be in terms of number of identical square units as 1 square unit, 2 square units, 3 square units,... as $a^2 \times 1$, $a^2 \times 2$, $a^2 \times 3$, $a^2 \times 4$,... as two dimensional, but in terms of unidirectional linear magnitudes they could be $a\sqrt{1}$, $a\sqrt{2}$, $a\sqrt{3}$... in increasing order of magnitude. This series $a\sqrt{1}$, $a\sqrt{2}$, $a\sqrt{3}$ is equivalent to the representation of various configurations of one, two, three... dimensions in terms of their linear magnitude of side (instead of a) in the configurations in figs. 20, 21 & 22 where these linear magnitudes are in terms of diagonals of the

configurations as $2\sqrt{3}.\sqrt{1}$, $2\sqrt{3}.\sqrt{2}$, $2\sqrt{3}.\sqrt{3}...$. The representation in a plane of uni-directional linear, two directional square, three directional cube etc., as a dimensional concept is similar to increase in linear magnitudes of roots of increasing number as magnitude of identical square units. Whereas the number of square magnitude increase as $a^2.1$, $a^2.2$, $a^2.3...$ the corresponding linear magnitudes should become $a\sqrt{1}$, $a\sqrt{2}$, $a\sqrt{3}...$. Thus in the two approaches these are identical except that the magnitude of constant side of the unit square in one case (figs. 20, 21 and 22) is " $2\sqrt{3}$ ", in the other case (fig. 12) it is " a ". The two approaches towards increasing magnitudes—one following fig. 12 and the other following figs. 20, 21 and 22 etc. should be clearly differentiated and their real difference identified, which would throw light on the concept of magnitude in terms of dimensions (uni, di, tri...) which could be of far reaching consequences. Linear representation of three dimensional cubical continuum in terms of its diagonal is $a\sqrt{3}$, 'a' being side and the digit 3 is magnitude representing three dimensional concept of configuration. Similarly linear representation of two dimensional square continuum is by $a\sqrt{2}$ in which 'a' is the side and 2 being the magnitude of two dimensional concept of configuration involved in it. Following the same line of argument $a\sqrt{1}$ is the linear representation of a straight magnitude in a plane in which 'a' is the linear straight magnitude and 1 is the magnitude of unidimensional concept of configuration involved.

The above is illustrated in the following:

One square unit, two square units, three square units..

Linear magnitude is $\sqrt{\text{One}.1}$, $\sqrt{\text{Two}.1}$, $\sqrt{\text{Three}.1}..$
 $= \sqrt{1.1}$, $\sqrt{2.1}$, $\sqrt{3.1} ..(\text{A})$

The concepts of configurations as:

(One) line	(Two) line	(Three) line
(One) square	(Two) square	(Three) square
(One) cube	(Two) cube	(Three) cube

are equivalent to:

1^1	2^1	3^1
1^2	2^2	3^2
1^3	2^3	3^3

Their linear representation would be as:

$1\sqrt{1}$	$2\sqrt{1}$	$3.\sqrt{1}$
$1\sqrt{2}$	$2\sqrt{2}$	$3.\sqrt{2}$
$1\sqrt{3}$	$2\sqrt{3}$	$3.\sqrt{3}..(\text{B})$

Both in A and B perception of changes in magnitudes are brought out through a common platform or basis as linear magnitude.

In A .. magnitudes vary as co-efficient of 1.

In B .. magnitudes vary as power of 1.

In A .. magnitudes convey quantitative aspect.

In B .. magnitudes convey qualitative or intensive aspects.

In A .. Relativity in continuum of constant co-ordinate is quantity.

In B .. Relativity in continuum of different co-ordinates is quality.

The difficulty which is associated with obtaining a clear picture about the 4 dimensional concept lies in this aspect that our conventions and concepts of magnitude are derived from plane square continuum, the derived linear magnitude from which can be made applicable to define variations of magnitude that can take place in one, two or three dimensional ways with regular rectangular co-ordinates. The 4 dimensional cases require one more co-ordinate which cannot be easily defined in terms of unidirectional linear dimensional configuration derived from rectangular plane. The concept of magnitude for four dimensional configuration in terms of magnitude of the dimensional concept derived from plane rectangular continuum will have linear representation of 4 dimensional configuration which would be $a\sqrt{4}$ which is the linear magnitude of any 3 diagonals at right angles in the configuration of octahedron (forming 4 triangular pyramids). All the four cases mentioned above are at right angles i.e. rectangular magnitudes of which can be defined from magnitudes obtained from square configuration in plane continuum, except that in the first three cases the magnitudes of the dimensional coordinates are linear at right angles, whereas in the 4 dimensional cases, as would be pictured from application of same concept of magnitude obtained from plane continuum, the four coordinates are pyramidal instead of linear, i.e. 4 three dimensional rectangular quadrants (as shown in fig.39) in 4 dimensional space.

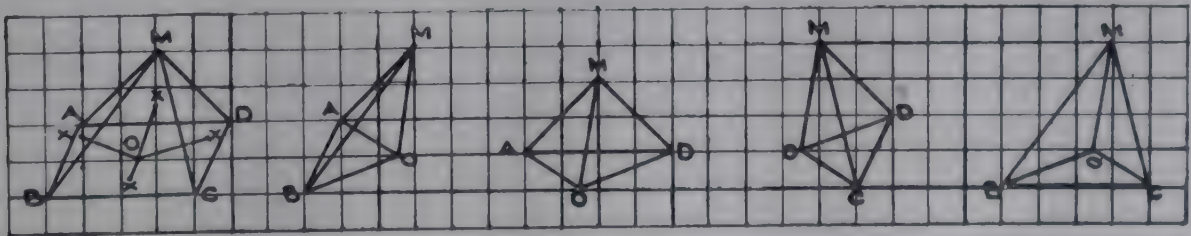


Fig. 39

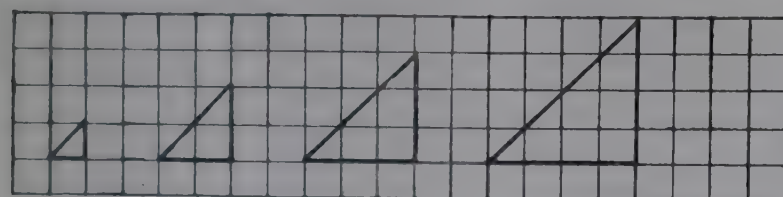
The above discussions should demonstrate the existence of two kinds of magnitudes. One kind of magnitude will vary within a constant reference frame or inertial co-ordinates and can be in the form of either linear continuum, square continuum, cubic continuum, or pyramidal continuum and so on i.e. within a constant configuration of continuum in which the magnitudes may vary. The other kind of magnitude may vary from one continuum to another (i.e. one inertial frame to another different) progressively. For the sake of illustration, in the first category would be the variation of magnitude in one continuum of constant reference frame of co-ordinates, say in a square continuum, the magnitudes may vary as

$$(0)^2, 1^2, 2^2, 3^2, 4^2, \dots$$

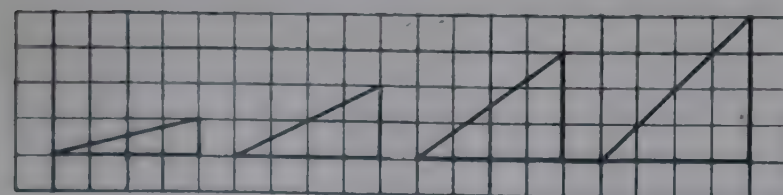
In the second category magnitudes may vary as, say, $1^0, 1^1, 1^2, 1^3, 1^4, \dots$

The nature of reference co-ordinate as an inertial frame would correspond to be the same as the variation of magnitudes in same reference frame of co-ordinate, say in a square co-ordinate as $(0)^2, 1^2, 2^2, 3^2, 4^2, \dots$

Instead of linear, square and cubical continuum of one, two and three dimensional co-ordinates, one could also consider the two dimensional triangular co-ordinates in which the magnitude may vary while retaining a constant gradient on the one hand and also the gradients may vary progressively from one frame to another on the other, as illustrated by fig. 40(a)



INERTIAL



NONINERTIAL

Fig. 40(a)

Variation of magnitudes within a particular inertial reference frame of co-ordinates and the variation of magnitudes involving different frames of co-ordinates are similar in concept with the numbers and digits referring to ordinals and cardinals. One can refer to one state or status in which the magnitude may vary. A magnitude

may vary in different co-ordinate system say, as in thermodynamic phases. In case magnitude may vary in one manner in first phase, it would vary in another manner in second phase, it would vary in different manner in third phase. The variation of magnitudes in any one particular phase would follow a certain constant or inertial co-ordinate relationship which may be designated by either one or two or three or four dimensional co-ordinate relationship following certain constant gradient as power or gradient like ratio of perpendicular to base etc. But the variation of magnitude involving different phases or configurations having different gradients or different coordinates will not be identical. For example, in a cubic continuum the magnitude varies as $1^3, 2^3, 3^3, 4^3, \dots$, in a 4 dimensional continuum it may vary as $1^4, 2^4, 3^4, 4^4, \dots$. Similarly, in a constant two dimensional triangular continuum in a plane having gradient of $1/4$, the magnitude will vary as $1 \times \frac{1}{4}, 2 \times \frac{1}{4}, 3 \times \frac{1}{4}, \dots$ or $\frac{1}{4}, \frac{2}{4}, \frac{3}{4}, \dots$. One point, therefore, is clear that in any particular continuum of configuration within a constant set of reference co-ordinate, magnitude may vary in quantity. But the change of reference frames from one phase to another, particularly from one state to another, or one level to another, progressively occurs in terms of intensity or quality or call it relativity.

Constant Velocity of Light

The velocity of light or radiation, whether and where it will be constant, will depend on the medium in which the radiation occurs. If the radiation occurs in a single phase having a constant reference coordinate of configuration of the continuum (medium) in which propagation takes place, the constancy may be expected. But if the radiation propagates through several media of different phases having different reference coordinates, obviously the velocity of radiation cannot be expected to remain constant, as the intensities in the different space time configuration will not be expected to remain constant in the path of propagation, during which progressively the units of configuration of space will also vary.

Michelson and Morley's experiment and its failure to detect ether drift has been explained in previous works.*
"All perceptible events are realised at a certain rate according to the relationships that are dictated by the constant frame of reference co-ordinate of the system or media in which the realisation is effected,—rate of realisation in a different frame of reference co-ordinate will be

* Relativity Analysed in the Light of the Theory of Universal Wave and New Theory of Unified Continuum—*Technol.* 5 (3A), (1968), 31.

different". This is the law of nature and should be applicable to all situations in phenomenal existence, in different fields or media of observations in our day to day experience.

The rate of change of properties of a constituent in a gas medium is not the same as the rate of change of properties of the constituent in liquid or solid medium. The fact that the environment influences the attitude of individuals would also follow from the same principle. One who has been used to remain in certain atmosphere and get seasoned or accustomed to the variable factors obtained in that atmosphere and thereby his attitudes and propensities are developed—the same in a different atmosphere in different set of circumstances will also develop his propensities and attitudes differently in conformity with the governing factors that are obtained in that different situation. Human beings in their continuum of existence between life and death are accustomed to only those situations and variable factors that are met with during the existence of life.

The nature of existence of the same before birth or after death will not be same. The existence of life, if that would exist before birth as well as after death, would belong to different phase or medium of existence of life from what a living man finds in the reference frame of co-ordinates of continuum between birth and death. Significance of Shri Aurovindo's "LIFE DIVINE" can be realised in this context. Validity or otherwise of the deductions would also be governed by whether the basic premises assumed for adoption to analyse a particular situation in conformity or not as has been explained in the present approach.

The ancient philosophies, in which the dominant feature of research has been made with respect to life, have emphasised the state of existence in different phases and from the logic of relationship that obtains between different phases in finite phenomenal existence have aimed to discover logically those relationships which would reveal the ultimate existence of animate life as the ultimate soul or Brahman (ब्रह्मन्). The main logic and the various postulates which have been deduced in the different Darshanas have concentrated in great detail in propounding these basic relationships. The system of Yoga and the methods prescribed to elevate life from its present state of existence towards realisation of higher states and progressively leading towards higher and higher elevation through different phases in the progressive status of cultivation of self have been the main theme which also follow the same law of nature as has been developed in the present approach.

Relationship between a total concept and the part

perceived, abstract aspect and concrete aspect, unknown aspect and known aspect of a thing—all these make the description of the thing complete. Merely taking those aspects of a thing or phenomenon which can be perceived or which are concrete, which can be known, do not make the complete picture of the thing. This has been the main lacuna in the approach of both Newton and Einstein in that: the former neglected the repulsion aspect and latter eliminated the unknown aspect from the basic postulates of their philosophies. Unless these approaches are modified and the other complementary aspects which should be taken into account and are realised the deductions of the modern science in general and physics in particular would not be correct. In ancient philosophies and Darshanas both these aspects have been emphasised. If there is a smoke, the inherent associated fire must also be taken for granted. Merely because smoke can be seen and is perceptible to senses, the absence of associated fire because it is not seen, cannot be justified. This method of deduction and ascertaining the relationship between the two aspects has been the main objective in the different systems of Darshanas and their philosophies.

(6) Magnitudes in Radial Development and Orbital Development

The nature of variation of magnitudes along inertial co-ordinates and the nature of variation of magnitudes involving different co-ordinate systems are similar in concept with nature of development of spherical surfaces with progressively changing radii. The equi-potential surfaces, as has been termed in the previous works, are similar to inertial coordinates at different spherical surfaces at different radial distances from the centre. The magnitude may vary orbitally pertaining to each spherical surface of increasing magnitude and magnitude also can vary radially traversing equipotential surfaces. The variation of magnitude traversing different spherical surfaces of varying magnitudes is equivalent to variation of magnitudes covering different non-inertial coordinate systems. [fig. 40(b)]

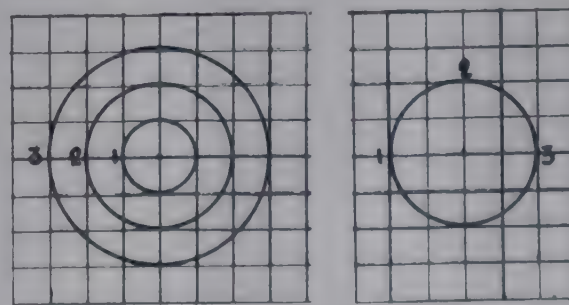


Fig. 40(b)

Radial variation and orbital variation of magnitudes are not identical. Suppose a quantity of a thing is having the property of possessing emanation from a point of position. If that quantity is condensed or intensified to a point of position wherefrom that quantity of entity would emanate then different distributions at different radial distances along the spherical surfaces will occur. Intensity of distribution of the same entity at different spherical surfaces will progressively decrease as the spherical surfaces will increase, though the quantity may remain constant. If the emanation is continuous then a potential gradient of distribution of the entity will take place from one spherical surface to another in the direction of increase of spherical surface or radius. At each radius at the corresponding spherical surface the corresponding intensity of distribution of magnitude may vary. The cumulative sum total of distribution upto a spherical surface would be of one kind when the sum total of the magnitudes will be counted in radial direction covering the sum total of distribution of all the spherical surface at increasing distances from the centre. The variation of magnitude at each orbital i.e. spherical surface will be of

another kind, like that in an inertial co-ordinate system.

The idea can be illustrated in a square continuum in a plane. Here, as we have shown before, increasing magnitude of squares in 4 directions can take place in a square continuum in two manners. In one manner the continuum may start with a square. In the other alternative, it can start from a point of position. The first mode will follow: 1^2 3^2 5^2In the second mode the magnitude of squares will follow: 0^2 , 2^2 4^2 , 6^2These are cumulative radial developments. The orbital development in the first case will be $1 \times 1 \times 8$, $1 \times 2 \times 8$and in the second case will be 1×4 , 3×4 , 5×4Since the square continuum is the projected configuration of 4 dimensional tetrahedral emanation in a plane, the evolution of energy matter in the universal context should also conform to these modes of emanation, and it should follow similar radial and orbital developments. This will be applied to periodic classification of matter in the next section which would clarify the development of matter elements in periodic classification, by both radial and orbital developments and distribution of electrons in specific orbits.

CHAPTER 6

Square Continuum and Electronic Development of Atomic Structure — Nature of Energy Matter Relationship

(1) Periodic classification of matter elements in Atomic Continuum, Nos. of electrons in atomic orbits in the present theory

In square evolution in a plane continuum there are only two modes in 4 directions. First mode starts with one evolved square and second mode starts from a point of position; these are:

$1^2 \ 3^2 \ 5^2 \ 7^2 \ \dots\dots\dots$ and

$0^2 \ 2^2 \ 4^2 \ 6^2 \ 8^2 \ \dots\dots\dots$ respectively.

Progressive orbital development of numbers of squares in the first mode is

8, 16, 24, 32.....

and the orbital developments in the second mode is
4, 12, 20, 28, 36.....

In the first mode the progressive sum total making perfect squares upto the orbits are—

1, 9, 25, 49—for corresponding development of orbitals at 1, 8, 16, 24———. Similarly, progressive sum totals making perfect squares upto orbitals in the second mode are—

4, 16, 36, 64....for corresponding orbital developments at 4, 12, 20, 28.....

This is illustrated in figs. 41(a), (b)

The progressive development of elementary atomic matter intensities and arrangement of electrons in orbits in the periodic classification of elements exactly conform to square evaluation in the second mode, which has been

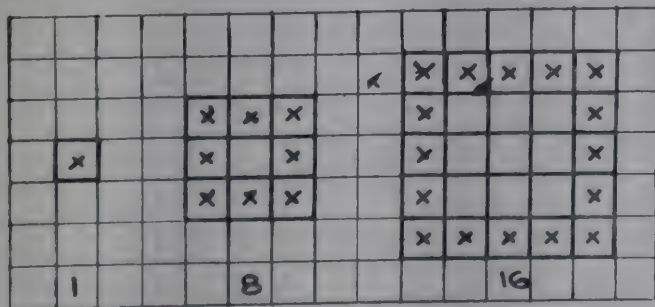


Fig. 41(a)—Starting with Square Unit Orbital Development in First Mode

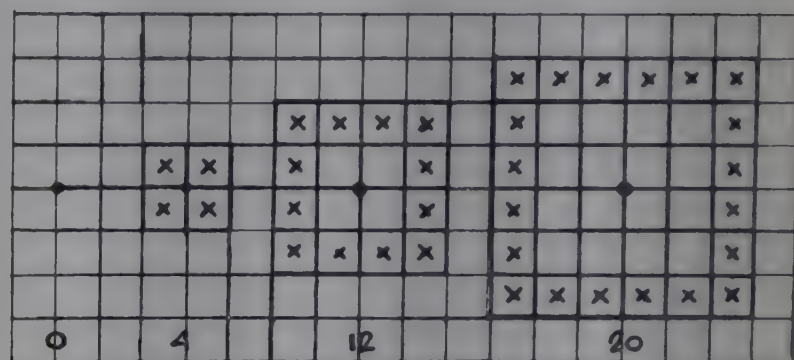


Fig. 41(b)—Starting with Point Position Orbital Development in Second Mode

known and was explained in the previous section,

as $0^2 \ 2^2 \ 4^2 \ 6^2 \ 8^2 \ \dots\dots$ and which in terms of opposite pairs would be 2,2; 8,8; 18, 18; 32, 32;

0, 4, 12, 20, 28....which in terms of opposite pairs would be as 2,2 6,6 10,10, 14,14

Progressive cumulatives according to which would be as

0 2 4 12 20 38 56....These also should be same for the various inert gases (including neutron) in order of increasing atomic matter intensities, as

0	2	4	12	20	38	56	88
photon	n	He	Ne	A	Kr	Xe	Rn

In terms of atomic numbers in the intervals are:

2—2, 8—8 18—18 32—32

These arrangements of electrons in orbits with progressive increase of atomic intensities of matter as per the present theory has been explained in detail in previous works.*

It would be obvious that as far as the elementary matter evolution is concerned the cumulative development of atomic intensities as well as nos. of electron in orbits follow the second mode of square evolution in a plane.

* Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol. 5* (2A) (1968), 64-65.

(2) What should be the Status of Energy in Association with Matter Evolution?

But it remains to find out the quantitative nature of associated energy with which the elementary matter must remain in equilibrium in its progressive development in the continuum. This is the vital enquiry, because herein lies the implication of the aspect of Einstein's ignoring the unknown aspect and Newton's gap. In their approach there is absence of any quantitative relationship of numerical or geometrical reference to energy/matter equivalence incorporating their intensities in the relationship, except mere statements of *status of energy levels*, corresponding to properties of electron to which they belong in quantum mechanics.

In the configurations of square evolution in plane continuum there are only two modes permissible in 4 directions and no more and the two modes are opposites. One mode follows squares on odd series, the other on even series. Energy and matter are opposites in the present theory. If, therefore, one mode is found to conform to matter evolution, the other E, about which little is known, should have something to do with the other mode which is its opposite. Modern science however experiences that matter cannot be without intimate association with energy (ante matter), which is its opposite. Therefore, energy should have something to do with the first mode in evolution as square concept in a plane, since that is the only complementary opposite arrangement permissible in plane square continuum.

A logical deduction could be that, since energy is first as cause, matter is next or subsequent derived, and since they are opposites (if that be accepted) then if and when energy appears in one square where M should be nil, then subsequently where E assumes 9 squares matter would assume 2^2 or 4, and progressively when E would assume 25, M would be 16 and further when E is 49 M would be 36 and so on.... Thus a controversy arises here as to whether:

E would be $1^2, 3^2, 5^2, 7^2, \dots$
or $2^2, 4^2, 6^2, 8^2, \dots$

when corresponding matter would be $0^2, 2^2, 4^2, 6^2, \dots$

Since previous and subsequents are also opposites like

E— $2^2, 4^2, 6^2, 8^2, \dots$

M— $0^2, 2^2, 4^2, 6^2, \dots$ just as $1^2, 3^2$

$5^2, \dots$ is opposite of $2^2, 4^2, 6^2, \dots$ and since the matter evolution has been realised as $2^2, 4^2, 6^2$ and that of energy has not been realised in the same pattern, it is essential to find out what would be the nature of simultaneous evolutions of E and M in plane continuum of squares by configurations representing the two evolutions.

In the previous works by the author it has been assumed that when $E=2^2, 4^2, 6^2, 8^2, \dots$ the matter would progressively develop as $M=0^2, 2^2, 4^2, 6^2, \dots$ in sequence.

Data from experience are not available as to know what it should be; whether E would correspond to

$1^2, 3^2, 5^2, 7^2, \dots$ when M would be

$0, 2^2, 4^2, 6^2, \dots$ or E would correspond to

$2^2, 4^2, 6^2, \dots$ when M would be $0^2, 2^2, 4^2, 6^2, \dots$

Relationship of spatial configurational aspects of energy vis-a-vis positional configurational aspects of elementary matter atoms are not known, except that the electrons form parts of atoms but do not constitute the space surrounding them, because another dimension photon constitutes space as energy radiation.

Interpretation from spectral lines many of which are diffused or perversely oriented, but the observations from those have led to the conclusions which form the basis of modern science, may not cover the complete picture.

Then in that case why not interpret from plane square continuum or isotropic configurations of positions in 4 directional space time continuum and deduce the probable basis in which the two opposites are involved?

For example in a plane unit squares constituting it are identical. In this, evolution of any kind should also be perfect so long as nothing other than the plane and position determining square is interfering. In that case results of observation in any mode will not involve any imponderable and arbitrary assumptions and the deductions therefrom could be correct.

In this background analysis in a plane square continuum in 4 directions when $0^2, 2^2, 4^2, 6^2, \dots$ denotes perfectly matter significance in evolution, the other and the only other possible alternative modes viz. $1^2, 3^2, 5^2, \dots$ or $2^2, 4^2, 6^2, \dots$ should have direct relationship with matter and energy. Hence the alternative configurations for E should be either $1^2, 3^2, 5^2$ or $2^2, 4^2, 6^2, \dots$ when M would be $0^2, 2^2, 4^2, 6^2, \dots$. It may be noted that acceptable correctness of interpretation of spectral lines as sharp, principal, diffused and fundamental varies from author to author.

In a square continuum of identical unit squares and positions interpretation of a certain aspect which could be obvious one and which could be independent of interpretations of individuals, there could be only one interpretation and there could be no distortion or approximation involved in deriving the result of observation in the process of assessment of the configuration being sharp, principal, diffused or fundamental—interpretation can be only one.

One has to know, what the configuration starts with

and what that ends upto and through what that traverses! To repeat this one must be sure about what it starts with, what it ends to and what it passess through.

In the case of a rectangular hyperbola it is not clear what it starts with and to what it ends up and what it passes through. Relative coordinates indeed are involved but their starting state, equilibrium state and finishing state should be known.

Cognisable spectral lines occur from what is projected on plane through lens of an apparatus. Whereas the tetrahedron to square projection on a plane is direct without involving any interfering medium which normally brings in imponderables or approximation; in the absence of that, interpretation of results from plane square continuum should be direct, since that does not involve the imponderables of that intervening medium.

Spectral lines for hydrogen are known in a certain manner, but, what are the spectral lines of photons and for that matter of neutron in the same manner?

(3) Square Continuum Representing Evolution in Plane and Deductions Therefrom in Ancient India

This aspect has been dealt with in some detail in previous works*. It was mentioned in the same work, that the concept of increase in magnitude in a continuum as could be interpreted from the continuum of identical square units in a plane was realised in India in ancient times. The two opposite modes only are possible in continuum of squares of identical units in a plane. These configurations are even now available in ancient scriptures under the nomenclature of Yantras and Chakras, which formed the origin of development of not only science and philosophies, but also were applied to in the religious domain in meditation, worship etc. Even now in many important temples in this country these Yantras and Chakras could be found imprinted on the floor, ceiling, and walls of the temples**. The evolutionary configurations in square continuum in a plane representing the two opposite modes were indicated in fig. 27, 28, 29 and 30 of *Technol. 5* (2A) (1968)—as already mentioned before. Some figures are reproduced below for ready reference and explanation (figs. 42 and 43).

Figs. 42 (a), (b) represent configuration of square evolution in four directions as $0^2, 2^2, 4^2, 6^2, \dots$

* Appraisal of Basic Concepts of Modern Science: Kinetics, Thermodynamics, Atomistics, Quantum Statistics in the Light of the Theory of Universal Wave & New Theory of Unified Continuum—*Technol. 5* (2A) (1968), 43-56.

** Ibid. idem, 55.

The configuration in fig. 43 represents square evolution as $1^2, 3^2, 5^2, 7^2, \dots$ starting with a square in 4 directions. The magnitudes of squares in configurations in figs. 42(a) and 42(b) start from a point O as $0^2, 2^2, 4^2, 6^2, \dots$. Squares in fig. 43 start from 1 evolved square and those in figs. 42(a) and 42(b) start from point of position.

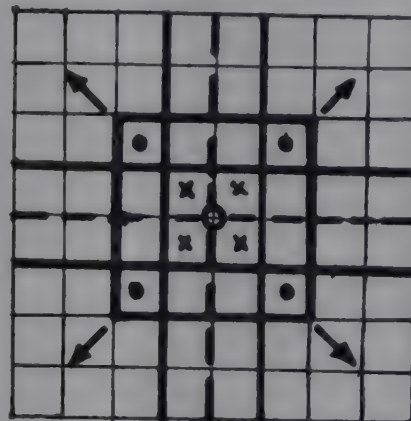


Fig. 42a

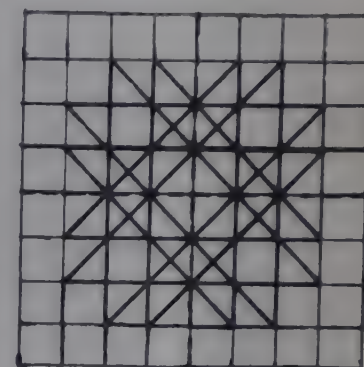


Fig. 42b

The fig. 42(a) is a simplified version of fig 42(b). It shows the square evolutions in 4 directions in simple manner. In each direction the magnitudes develop as $0^2, 1^2, 2^2, 3^2, 4^2$ starting from central position O in fig. 42(a), (b). But the development of magnitudes of squares in one direction in the mode of evolution in fig. 43 starting with an evolved square as the central square 'O' would also be $1^2, 2^2, 3^2, 4^2, \dots$ as may be seen from the configuration in fig. 43.

The two configurations are opposite in nature. Both the configurations show the square evolutions in sequence. The one in fig. 43 as $1^2, 3^2, 5^2, \dots$ follows the

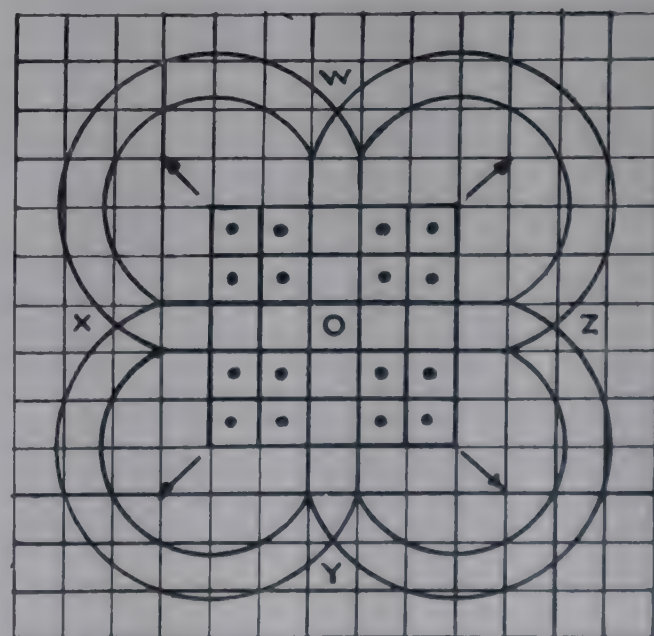


Fig 43

general formula $(2X+1)^2$ in 4 directions. The subsequent evolution of dotted squares as $0^2, 2^2, 4^2, 6^2, \dots$ which follows the general formula $(2X+0)^2$ and are in 4 directions can also be discerned from fig. 43. The outer circular links in each direction incorporates the square evolution involving the central square (0) following $1^2, 2^2, 3^2, \dots$ in one direction, the inner circular links indicate subsequent square evolution (dotted squares) in one direction which excludes the central square and follows $1^2, 2^2, 3^2, \dots$ in one direction. If the evolution would be considered simultaneously in 4 directions, then the first square evolution is $1^2, 3^2, 5^2, \dots$ and the magnitudes in the subsequent or next mode in sequence are $0^2, 2^2, 4^2, 6^2, \dots$ (these squares are with dots). The circular links which are found in the temple configurations as in fig. 43 strictly are not part of the actual square continuum but are intended to indicate the co-ordinates of the two evolutions in sequence (outer one is first and inner one is subsequent). It may be recalled that the evolution of digits and numbers which has been explained from configuration of square continuum in fig. 4 in a previous section also shows exactly identical mechanism of progressive development in sequence towards higher magnitudes in phases as unit, 10th, 20th, 30th and so on.

In fig. 43 if one would consider only the development in one direction it may be noted that one could interpret that while the first square development occurs as $1^2, 2^2, 3^2, 4^2, \dots$ in one direction, the subsequent corresponding development in one direction could be as $0^2, 1^2, 2^2, 3^2, 4^2$.

The configurations given in figs. 42 and 43, as found in ancient Indian temples, however, do not specifically mention which configurations refer to which specific dimensional evolutions in sequence as was known to have been associated with these in ancient times, viz. with Purusha and Prakriti in the Sankhyya Darshana. There could be one explanation that the configuration in fig. 43 is the evolution of Purusha as first and Prakriti as the subsequent, both in one configuration. One could also suggest that configuration in fig. 43 refers only to Purusha evolution and fig. 42 to Prakriti evolution.

If the configuration in fig. 42 would incorporate both Purusha and Prakriti evolution then the nature of the evolutions representing the two modes in succession can only be

4, 16, 36, 64	for the first dimension
0, 4, 16, 36	for the subsequent dimension.

which is the same as:

$2^2, 4^2, 6^2, 8^2$
$0^2, 2^2, 4^2, 6^2$

Energy and Matter Evolution

These two opposite modes of configurations could also reflect the nature of evolution of energy and matter in their sequential development in association with one another, the former for energy and latter for matter in sequence. The configuration which would conform to matter evolution as $0^2, 2^2, 4^2, 6^2, \dots$, can be either in fig. 42 or in fig. 43. If it is fig. 42, the progressive development of matter (sequence) squares would be those that are with dots in succession. The problem is what should be the nature of association of the squares in the configuration representing the energy aspect? From fig. 43 the association can be $1^2, 3^2, 5^2, 7^2, \dots$ which involves the central square for the first and $0^2, 2^2, 4^2, 6^2, \dots$ which excludes the central square and starts with squares with dots, significance of which has been explained before. But in fig. 42 the matter association necessarily has to be as $(0)^2, 2^2, 4^2, 6^2, \dots$, while the corresponding energy association in the combination would be as $2^2, 4^2, 6^2, \dots$ the simultaneous matter would be $0^2, 2^2, 4^2, 6^2, \dots$. This is indicated in fig. 42 in which the first four square units represent energy as 2^2 (marked with +) with zero association of matter. In case of next magnitude for energy which would be 16 or 4^2 there would be 4 or 2^2 (squares with dots) matter association in the configuration.

(4) Explanation of Energy Matter Relationship in Evolution

The basic premises on the manifestation of the continuum of four dimensional universal space in this theory are:

1. It is isotropic and tetrahedral in concept.
2. Square continuum in a plane represents projected picture of four dimensional space by being converted into a two dimensional square continuum in a plane.
3. Analysis and deduction from square continuum in proper perspective should be applicable to four dimensional space time continuum.
4. Space itself is energy. Matter is position in space, its indistinguishability or distinguishability depends on its occurrence in the nature of its phases in which it exists.
5. So long as universe is there space or energy must be there—its absence means absence of the universe itself. Absence of matter, i.e. its nil magnitude can only occur in the background of pure space.
6. In the finite universe, energy or space must always be present in its varying intensities in which matter can co-exist in its magnitudes of intensities varying from nil to highest.

7. Space is indivisible whereas matter is divisible or distinguishable in space. If space is odd, matter should be of even concept. Energy is first concept, matter is subsequent in manifestation in association with energy.

The following analysis of energy matter relationship is offered in the above background premises.

The two opposite natures of configurations in figs. 42 and 43, it appears, are intended to incorporate in one configuration the developments of magnitudes of squares in the two opposite modes to be conveyed by magnitudes of identical squares.

It is intended here to explain the square evolution in alternative modes which simultaneously incorporate the two opposite aspects like energy and matter in the same configuration.

In the theory of universal wave the two opposite dimensions energy and matter have opposite characteristics in every respect.

Energy creates space concept in 4 isotropic directions. Matter dimension is a concept whose tendency is to occupy a point of position in the created space. Thus when space is created first by energy as square in 4 directions and the first square is formed, the subsequent dimension matter association with it is in an undefinable association conveying no distinct position yet occupied by it within the configuration of first square unit. After the first unit of square configuration has been generated by energy and subsequently 3^2 units would have been generated by it in 4 directions, the matter subsequently creates 4 distinct positions (each from every three evolved directions). Thus by the time the 4 matter positions are formed the original or first tetrahedron has further emanated space towards bigger magnitude equivalent of 3^2 unit squares. This concept has been attempted to be explained by fig. 44.

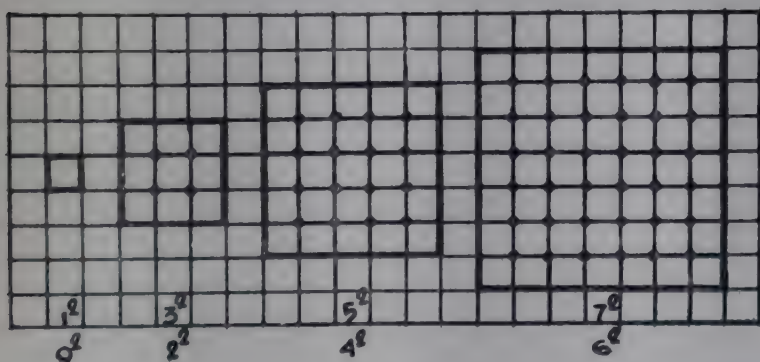


Fig. 44

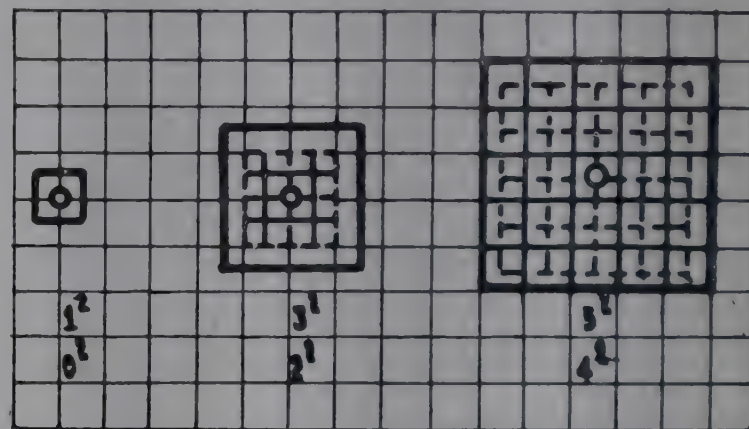
The first square formed by energy has no distinct positions within it as no matter positions have been formed. When the square magnitudes attain 3^2 , within

this square configuration there are 4 distinct positions within the evolved square due to energy. When square magnitude due to energy increases further to 5^2 , there will be 16 distinct positions within the 5^2 configuration. In this way if energy represents squares magnitude in terms of squares and matter represents number of positions within the generated square then the energy and corresponding matter evolution associated in the combination will be as follows:

$1^2, 3^2, 5^2$ (in terms of squares).

$0^2, 2^2, 6^2$ (in terms of positions within the generated square).

The second alternative mode in which the two opposite developments would be represented by squares of identical units (not by square and point of position) has been indicated in fig. 45. In this the squares with conti-



Squares with Full Line $1^2, 3^2, 5^2$
Squares with Dotted Line $0^2, 2^2, 4^2$

Fig. 45

nuous lines indicate square evolution starting with a central square 0 as $1^2, 3^2, 5^2, \dots$. Starting from the centre of the central square, the square mode of evolution following the series $0^2, 2^2, 4^2, 6^2, \dots$ are indicated in dotted lines. In this configuration the magnitudes of square units: one with continuous lines and the other with dotted lines are identical. But when the first square 0 has been developed no complete square within this by dotted lines has appeared. When the magnitude of second squares with continuous lines develops to 9 i.e. 3^2 , the 4 complete or distinct squares with dotted lines have appeared within it. Similarly when third square magnitude with continuous lines is 5^2 the developed square with dotted lines is 4^2 and so on. In this, it may be noted that the development of the higher magnitudes in both the modes would correspond to $\frac{X+(X+2)}{2}$; when $X=1, 3, 5, \dots$ the magnitudes of the evolved squares are $2^2, 4^2, 6^2$. When $X=\text{even numbers}$

as 0, 2, 4, 6, the magnitudes of the evolved squares would be as $1^2, 3^2, 5^2, \dots$. In this configuration resultant square magnitude in one (odd or even) mode is equal to square of half of the sum of the roots of previous and subsequent squares in the opposite mode. It is significant to note that the magnitudes of the squares in any mode is not just the magnitude of squares or their roots are not just the average of previous and subsequent equal, and opposite, but relative to the present one is less, the other is bigger. The average is not an average of linear magnitudes of identical unit in the direction of development, but is the average of evolved magnitudes of squares in the direction of accelerated development.

From the above the following deductions about generation of even or odd squares in the continuum would be clear.

In the development of square magnitudes in the odd modes (also in the even mode) the magnitude of square of half of the sum of the roots of previous and subsequent squares would be represented by

$$\left[\frac{\sqrt{1^2} + \sqrt{3^2}}{2} \right]^2 = (1+1)^2 = 2^2$$

$$\left[\frac{\sqrt{3^2} + \sqrt{5^2}}{2} \right]^2 = (3+1)^2 = 4^2$$

$$\left[\frac{\sqrt{5^2} + \sqrt{7^2}}{2} \right]^2 = (5+1)^2 = 6^2$$

These can be represented by general algebraic formula as:

$$\left[\frac{\sqrt{a^2} + \sqrt{(a+2)^2}}{2} \right]^2 = (a+1)^2$$

In this the values of 'a' are in increasing magnitudes of odd numbers in sequence as 1, 3, 5, 7, ... and the roots of resultant squares are even as 2, 4, 6.

Similarly when 'a' would be even the resulting squares would be on odd.

$$\left[\frac{\sqrt{0^2} + \sqrt{(0+2)^2}}{2} \right]^2 = (0+1)^2$$

$$\left[\frac{\sqrt{2^2} + \sqrt{(2+2)^2}}{2} \right]^2 = (2+1)^2$$

$$\left[\frac{\sqrt{4^2} + \sqrt{(4+2)^2}}{2} \right]^2 = (4+1)^2$$

If we now consider the square continuum in terms of square units of even numbers (which represent matter phase in the present theory) then, therefrom we can find the general algebraic formula for orbital develop-

ment with progressive development of squares on even numbers representing matter. For example, when matter is nil orbital development of matter is nil. For matter next development is 2^2 followed by $4^2, 6^2, \dots$. The corresponding numbers of orbital square units are 0, 4, 12, 20, 28, ... having corresponding full squares as $0^2, 2^2, 4^2, 6^2, 8^2, \dots$. This algebraic formula for development of orbital squares in the series would be represented by

$$(a+1)^2 - (a-1)^2$$

which gives (a being odd) 0, 4, 12, 20, 28, ... as numbers of squares in orbits of the full squares of increasing magnitudes. This has been shown before in fig. 41(b).

These numbers of orbital squares in their opposite magnitudes would be 2 opposite pairs, 6 opposite pairs, 10 opposite pairs, 14 opposite pairs and so on.

This exactly correspond to numbers for s, p, d, f, ... in quantum arrangements of electrons in orbits of atoms, which will be mentioned later.

The significance of this particular deduction would be obvious from the fact that the development of increasing magnitude of odd square space, which corresponds to energy, follows $1^2, 3^2, 5^2, 7^2, \dots$ (figs. 44 and 45). The magnitudes of matter significance which represents points of position in fig. 44 and number of dotted squares in fig. 45 are produced as resultants while the square magnitudes representing energy, changes (emanates) from previous to subsequent generating the resultant as matter squares.

Thus the energy squares while changing from 1^2 to 3^2 generates the resultant even matter as 2^2 . Similarly the energy squares while changing from 3^2 to 5^2 generates the resultant of even squares for matter as 4^2 and so on and so forth.

Theoretically, in the above algebraic formula 'a' could also be even number in numerical magnitude of squares, in which case, the resultant squares would be squares of odd numbers of increasing magnitude. But in the energy matter evolution the generation of even squares from odd squares only is relevant because of the following reasons:

Energy is fundamental and is the cause and matter is the effect. Energy is space (here it generates first square space of 1^2) which is generated first and the matter is subsequent which generates positions from the generated space as per fig. 44. In another way when the magnitude of energy of odd square space changes (decreases from prior intensity to next in odd series) from previous to next, it generates an even resultant at

equilibrium as a new phase of even squares attributed to matter significance.

Squares on odd magnitude representing cause states, generate squares on even magnitude representing subsequent or effect states.

It is interesting to note that, as a corollary from the above deductions while 1 is always an odd function, zero is an even function which would be generated as "square of half of the sum of the roots of $(-1)^2$ and $(+1)^2$ ", in other words:

$$\left[\frac{\sqrt{(-1)^2} + \sqrt{(+1)^2}}{2} \right]^2 = 0$$

or

$$\left[\frac{(-1) + (+1)}{2} \right]^2 = 0$$

In the above premises in terms of square magnitudes energy evolution follows $1^2, 3^2, 5^2, \dots$ and square magnitudes representing matter evolution follows $0^2, 2^2, 4^2, 6^2, \dots$. Since energy and matter evolutions occur in sequence while progressive evolution of space occurs with decreasing energy intensity, in a common background of square space evolution which is a projection, in a plane, of tetrahedral space evolution in 4 directions in space, the relationship between the two types of evolution as $1^2, 3^2, 5^2, \dots$ and $0^2, 2^2, 4^2, 6^2, \dots$ for energy and matter respectively should lead to the establishment of energy and matter relationship. The dimensional significances of the symbols E and M, it should be remembered, represent intensities.

(5) Variation of energy intensity with progressive development of space (in terms of sq. space) and Energy and Matter relationship

The phenomenon of creation of space (4 directional) by energy emission when projected in a plane, assumes the configuration of increasing magnitudes of squares of odd numbers in a plane, as

$$1^2, 3^2, 5^2$$

The first start is made with one square unit which contains all the energy. When this first square unit develops into 3^2 , i.e. 9 square units, the energy which was contained in the first square unit is now distributed amongst the 9 square units, which means that if the intensity of energy in the first evolved square unit was $1/1$, when the nine square space units have been developed the intensity of energy becomes $1/3^2$. Similarly when the magnitude of square space develops into 5^2 , the energy intensity becomes $1/5^2$. Thus the progressive variation of the intensities of energy E, as the magnitude

of emanated square space due to energy increases, would follow the series in sequence.

$$1/1^2, 1/3^2, 1/5^2, 1/7^2 \dots (X_1)$$

The development of magnitude of matter significance along with creation of energy space (obviously in terms of square space), however, follows in opposite direction to that of energy. When energy created the first square the matter content was nil. Thus the intensity of matter in that was $0/1^2$. When energy emanated space changes from 1 to 9 square units magnitude of matter development is 2^2 . Thus the intensity of matter distribution within the generated space would be $2^2/3^2$. When the generated space magnitude would be 5^2 , the magnitude of matter generated is 4^2 and the intensity of generated matter within the generated space would be $4^2/5^2$ and so on.

The progressive development of corresponding matter intensities relative to energy space magnitudes would thus be represented by

$$0/1^2, 2^2/3^2, 4^2/5^2, 6^2/7^2 \dots X_2$$

In the theory of universal wave, energy and matter are the two main constituents of the inanimate universe. In all the manifestations both must remain in combination, but they vary in their intensities in combination from one manifestation to another. The variation of their intensities in combination is such that sum total of their intensities would remain constant. This is the principle of conservation of energy and matter. It is not their quantity in their combination which matters, but it is the intensity of both in combination that matters. It has been shown before that with the evolution of energy space the intensity of energy in space varies as:

$$1/1, 1/3^2, 1/5^2, 1/7^2 \dots X_1$$

and the intensity of matter varies as

$$0/1, 2^2/3^2, 4^2/5^2, 6^2/7^2 \dots X_2$$

The sum totals at the different states however are not constant. For example:

$$1/1 + 0/1 = 1$$

but $1/3^2 + 2^2/3^2 = 5/3^2$ which is less than 1;

Similarly,

$$1/5^2 + 4^2/5^2 = 17/5^2 \text{ which is also less than 1.}$$

The deficient or unrealisable portion would be

$$0/1, 4/3^2, 8/5^2, 12/7^2 \dots X_3$$

corresponding to the intensity of M in the series (X_2) and intensity of E in (X_1) in the above. The development of energy matter in combination expressed in X_1, X_2

and X_3 can be represented by the algebraic formulae as

$$\frac{1}{(a+1)^2}, \frac{a^2}{(a+1)^2} \text{ and } \frac{2a}{(a+1)^2} \text{ respectively; sum}$$

total at any corresponding state in the series X_1 , X_2 and X_3 would be $\frac{1+a^2+2a}{(a+1)^2} = \frac{(a+1)^2}{(a+1)^2} = 1$, in which 'a' is even.

The part contributed by matter intensity development would be given by algebraic formula,

$$a^2/(a+1)^2$$

the corresponding energy intensity development can be represented by $1/(a+1)^2$

and the unrealisable part in the energy matter combination to retain principle of conservation would be

$$2a/(a+1)^2. \text{ In all these cases 'a' is even.}$$

It is now necessary to explain these three vital aspects of energy and matter combination in the universal context. In the configuration of the universal wave there are three zones. The central zone within the critical equilibrium state is the pure energy zone and outside the critical is the heterogeneous zone in which two phases co-exist in equilibrium. In the condensed phase which corresponds to $a^2/(a+1)$ while energy intensity decreases, the matter intensity increases. In the depleted phase which corresponds to $2a/(a+1)^2$ the matter intensity decreases with decrease of energy intensity.

This resemblance is identical with what is experienced from thermodynamic data, viz. between the two critical states, liquid and gas (at critical temperature) and liquid solid critical temperature. Between these two limits only vapour and liquid exist. Neither solid phase nor superheated gas phase can have permanent existence in this phase. The vapour density (of the depleted phase) which corresponds to $2a/(a+1)^2$ decreases with decrease of temperature (i.e. energy intensity in the present theory—as $1/(a+1)^2$). In the condensed phase the liquid density which corresponds to $a^2/(a+1)^2$ increases with decreases of temperature between the two critical states.

Thus, the above algebraic formulae for energy-matter relationship satisfactorily explain not only the variation of thermodynamic properties of phases in equilibrium combination but also atomic matter development with progressive development of energy space in the Universal context. It should be noted that 2^2 , 4^2 , 6^2 ... correspond to the progressive development of electrons in elementary matter with increase of atomic number or atomic weight signifying increasing atomic matter intensities in periodic classification and this does not incorporate the aspect

$\frac{2a}{(a+1)^2}$ which corresponds to the surrounding equilibrium space with which the atoms at various stages of development would be in equilibrium combination. This aspect has not been understood in conventional approach and remains unexplained. This will be dealt with later.

Orbital Development

Let us now consider the orbital development. From figs. 44 and 45 it is easy to see that the orbital development of matter intensity magnitudes in the square space development is

$$0/1, 4/8, 12/16, 20/24 \dots X_4$$

The corresponding energy intensity variation is

$$1/1, 1/8, 1/16, 1/24 \dots X_5$$

The unrealised matter portion is

$$0/1, 3/8, 3/16, 3/24 \dots X_6$$

At each orbital state the sum of these three, it may be noticed, is constant and is equal to 1 at each stage in the series.

If one would consider the cumulative development of magnitudes up to the various orbital states excluding the first square unit then cumulative progressive development of matter corresponding to condensed phase would be

$$4/8, 16/24, 36/48$$

The progressive energy intensity development would be

$$1/8, 1/24, 1/48$$

and the unrealised phase of matter in the phase corresponding to depleted phase would be $3/8, 7/24, 11/48$.

It may be seen from X_4 in the above that the distribution in orbits follows the series 2,2; 6,6; 10,10; 14,14; which corresponds to electronic distribution in progressive development in elementary atomic matter as 2,2; 6,6; 10,10; 14,14. in the different orbitals in sequence. The cumulative development up to various orbits in sequence, which follows 2,4; 12,20; 38,56... also corresponds to what should be the correct atomic numbers of elementary matter atom in periodic classification of elements.

But the important aspect about the nature of equilibrium space with which the elementary matter atoms would be in equilibrium, i.e. the properties of space surrounding condensed phase of atomic configurations, and the nature of energy and matter significance which corresponds to the depleted phase in the heterogeneous zone of the universal wave (which corresponds to the

vapour phase surrounding the condensed liquid phase) in combination with that space and their relative magnitudes and the various atoms which should correspond to various atomic magnitudes corresponding to say $2^2, 4^2, 6^2 \dots$ are not clear in conventional approach.

It is contended that the space which should remain in equilibrium (corresponding to the vapour phase in equilibrium with condensed liquid at different temperatures as boiling points) with atoms of varying matter magnitudes should have also the corresponding matter intensity of the constituent of that space. If photon would be the constituent of that space then its matter magnitude should vary in surrounding equilibrium space as $4/3^2, 8/5^2, 12/7^2 \dots$ i.e. following the general formula: $2a/(a+1)^2$ in association with matter intensity development of the condensed phase as $2^2/3^2, 4^2/5^2, 6^2/7^2 \dots$ i.e. following general formula $a^2/(a+1)^2$. The corresponding energy intensity of photonic space would be as $1/3^2, 1/5^2, 1/7^2 \dots$ following general formula as

$$\frac{1}{(a+1)^2}.$$

The development of matter magnitude in the condensed phase of atomic configuration is associated with increase in matter intensity with decrease of energy intensity of space and follows the general formula $a^2/(a+1)^2$.

Whereas in the surrounding equilibrium space which should be in equilibrium at the various states in the series following the general formula $\frac{2a}{(a+1)^2}$, the space constituent would progressively decrease in matter intensity along with decrease of energy intensity of that phase while remaining in equilibrium with the condensed matter phase of increasing matter intensity.

If energy matter equivalence or energy matter relationship would be determined in totality the above relationship should be satisfactory which takes into account all aspects and phases involved in the combination which will be relevant and invariably present. If any aspect will be left out then the analysis would be incomplete, and deductions therefrom would be incorrect.

(6) Variation of matter intensity of photon along with energy intensity of distinguishable photonic space

It is clear from the above analysis that Einstein's energy matter relationship and equivalence is incomplete. The above shows that in matter and energy in combination in any manifestation, the sum total of their intensities will remain constant. But in different manifestations matter and energy will be in combination

in their different intensities. But sum total will have to remain constant.

If, however, the energy matter relationship in the depleted phase only is taken, it may be noted that, with increase of energy intensity of space the matter intensity of the space constituent also increases. Thus, the variation of intensity of energy and variation of intensity of matter of the space constituent (photon) surrounding condensed phase moves in the same direction. But they move in opposite directions in the condensed phase of atomic configuration. If only the former part, i.e. the variation of intensity of energy and the variation of matter intensity of only the constituent of surrounding space is taken in isolation leaving aside the condensed phase of atomic configuration with which the surrounding space must be in equilibrium, then Einstein's energy matter relationship as applied to photon could be valid. This analysis would therefore lead to a very important deduction that the matter intensity of photon of space which would remain in equilibrium with the elementary matter during the evolutionary process of their development, would have the highest value in space which would be in equilibrium with the first condensed phase (of lightest atomic matter) of atomic configuration of orthohydrogen. But from that state as the energy space emanation progressively occurs and increases in magnitude with progressive decrease of energy intensity of space progressive development of atomic condensed phase of higher atomic weights would have to be in equilibrium with space of decreasing energy intensity as well as decreasing matter intensity which would progressively be in equilibrium with the increasing development of matter intensity of atomic configuration. But the photon of surrounding space would have to have progressively decreasing matter intensity in the same direction. The conclusion would be that, space which would be in equilibrium with atomic matter with highest matter intensity (i.e., say highest atomic weight) would be in equilibrium with surrounding space which would have photonic constituents of space having least matter intensity.

We have mentioned before about the probable existence of photon in different phases having different matter intensities. The photons of space energy as radiation in modern statistics are thought of as particulates and are identical with one another but they are distinguishable. The photons of space, which would be in equilibrium with least matter intensity of atom, i.e. ortho-hydrogen, would be distinguishable identicals. But the phase of photonic space beyond ortho-hydrogen would be indistinguishable relative to phase of space

as is known, which remain in equilibrium with distinguishable atoms however less their matter intensities might be. We have already discussed the probability of phase of photon as indistinguishable phase. The difference between the two phases of photonic space would be one phase is like that of H_2O in vapour phase in equilibrium with liquid H_2O up to the critical point and the other phase is like that of H_2O in superheated gas phase above critical; up to the critical point H_2O vapour density increases towards the gas/liquid critical state and the density of H_2O in liquid phase decreases towards the critical. At the critical state, vapour and liquid phase densities become identical, above the critical they become one phase as indistinguishable which is superheated H_2O as gas phase in which the two distinguishables merge into one phase. Likewise, instead of H_2O , photon in the space which should be in equilibrium with elementary matter atoms up to the critical state i.e. at the ortho-hydrogen state beyond which atomic configuration of atomic nucleus vanishes and the equilibrium space phase of distinguishable photon will also vanish. Beyond that critical state neither atomic configuration nor distinguishable photon will be present. That phase of space which we have termed as indistinguishable photonic phase is like superheated phase of H_2O above its gas/liquid critical state.

In the context of evolution of distinguishable atomic matter from energy as space, indistinguishable photonic space cannot co-exist in equilibrium with any distinct developed atomic configurations starting with ortho-hydrogen downwards just as H_2O as superheated gas cannot co-exist in equilibrium with liquid H_2O below critical.

Statistical probability and improbability and for that matter certainty and uncertainty together must be assumed to be present and be associated in all universal manifestations for realisation of complete knowledge of the manifestations of the universe as a whole. To know the whole truth taking only one aspect which is perceived and leaving out the part which is not perceived cannot lead to acquiring knowledge of whole truth. This is an important postulate in the present theory. Therefore, the very starting premise of Einstein "if a thing is not observed why it is necessary to assume its existence"—cannot be correct and on this basis any approach to have quantitative knowledge of complete facts about any manifestation be it the nature of manifestation of energy matter or be it deduction therefrom of quantitative relationship between matter and energy etc. cannot lead to correct conclusion. In fact the issue seems to be so

obvious. To know any individual being in his completeness not only his known aspects but unknown aspects also are to be taken into account. For example, we have illustrated in previous works that to know a man in completeness, his known aspects—what can be seen, felt, heard and perceived along with those aspects which are not seen, not heard about him and which are not within perception and knowledge of observer,—those aspects must also be incorporated to define quantitatively completeness of the man. In fact, there cannot be any manifestation or phenomenon in the universe which will defy this postulate. In the deductions of energy matter relationship in the present theory derived from the relationships in square continuum (a^2+1) is not a complete square. To get the square perfected the portion $2a$ must also be added. Conversely $2a$ is not a complete square by itself, to this a^2+1 has to be added to get the complete square as $(a+1)^2$.

The exact nature of photon of space phase cannot be known without knowing its matter and energy intensity with which the other phase, i.e. elementary matter atomic phase will be in equilibrium association. Conversely the knowledge about an atom—its stability and energy intensity cannot be known without the knowledge of the property of the equilibrium associated space and the nature of photon constituting it.

We have been using the term photon of space of varying intensity and of matter which would be in natural equilibrium with elementary matter of varying atomic matter intensity. This requires some clarification since the concept is somewhat different from conventional ideas. Photon is a property of space which is similar to H_2O vapour surrounding liquid H_2O as the property of space phase surrounding liquid phase. Similarly, atoms are properties relating to positions in space. Just as H_2O in vapour phase varies in its vapour density with temperature while in equilibrium with liquid phase so also density of liquid phase varies with temperature while in equilibrium with its vapour phase. But the two variations are in opposite directions. On similar lines as has been discussed earlier, the characteristics of space which would be in natural equilibrium with the atoms in their atomic phases of varying atomic weights the constituent of space which is conventionally understood as photon will also undergo variation in its matter intensity.

The question is what is the nature of photon that will be in equilibrium with varying matter intensities of atoms. Will the photon of space phase always remain of constant matter intensity while the space will be in its natural equilibrium with the highest as well as least

atomic matter intensities or the photon will undergo change in its configurational property? What is meant here is to clarify that the photon as constituent of space can vary in its matter intensity retaining the property of photon just as H_2O in vapour phase varies in its matter intensity retaining the property of H_2O as entity.

Gas and vapour are space constituting phases. Different gas molecules make different gaseous space phases. Similarly, photon as generalised constituent of space phase, can have different modifications in a space of certain energy intensity as is experienced in space surrounding earth in equilibrium with matter entities that are present in the surface of the earth. In another atmosphere, say, that of sun or in the atmosphere of quassers the photon of space of those atmospheres may have different modifications also. In one case, space may constitute of conventional photon, in a different space it may be of proton radiation, neutron radiation, alpha particle and so on. The natural development in evolution of elementary matter starting from hydrogen towards the heaviest atoms have various stages of their development. These different atoms will be in the natural equilibrium with different kinds of space. The constituents of space, which would be in natural equilibrium with progressively developing atoms in the order of higher atomic weights, which in the present approach are generalised as proton, it could be in terms of photon as we know conventionally or in terms of its different modifications like, say X-ray, gamma ray, beta ray, proton ray, neutron ray and so on and so forth.

(7) Development of matter phases in progressive sequence forming continuum while energy progressively emanates space of magnitudes

In the following the presentation of this phenomenon as would be derived from square continuum in plane has been considered. Although this aspect more or less would be repetition of what has been already described in the previous sections, even then for the sake of further clarifications the discussions are repeated here in a somewhat different manner.

Fig. 46 as usual represents progressive development of Energy quares starting with:

- E_1 which is 1^2
- E_2 which is 3^2
- E_3 which is 5^2
- E_4 which is 7^2
- E_5 which is 9^2

At the E_1 state energy is represented by 1^2 unit. At the E_2 state the total square developed is 3^2 or 9, but the orbital development is 8. From E_2 to E_3 state total

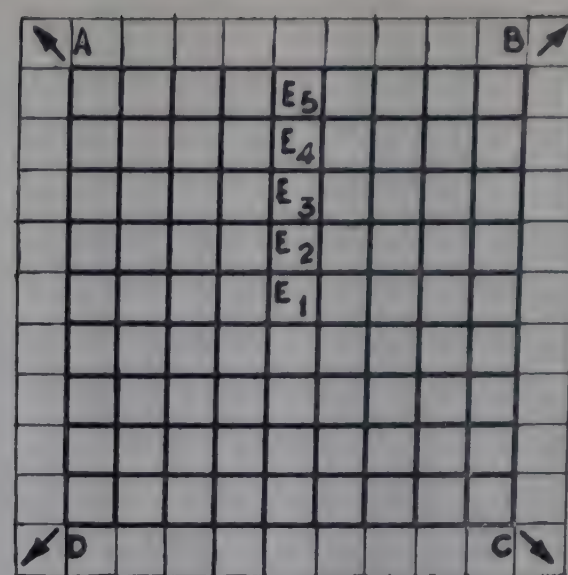


Fig. 46

space developed is 5^2 or 25, but the orbital development is 16. Similarly at E_4 state the total square development is 49 square units or 7^2 , but the orbital development is 24 and so on.

In fig. 47 in the same background of square continuum as ABCD in fig. 46, the progressive development of matter has been shown. At the state E_1 , the matter phase is represented by M_0 (i.e. nil matter). At E_2 state matter phase is represented by M_1 . Similarly for E_3 , E_4 , E_5 states, matter development would be M_2 , M_3 , M_4 respectively. From the development of squares in the continuum shown in fig. 47, it would be clear that at the highest energy intensity when E_1 was represented by the first square unit space, the distinguishable matter phase in that energy state was 0. But when energy further develops the square space E_2 from E_1 , M —the distinguishable matter in that energy phase—becomes $4M_1$. When energy has developed to E_3 state, total develop-

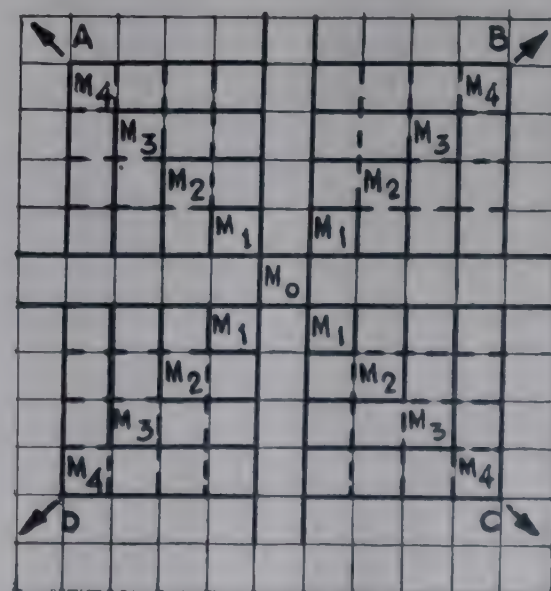


Fig. 47

ment of M is $4 \times 4 = 16$, but the orbital development of M from M_1 to M_2 is 12. At the energy state E_4 , matter development is up to M_3 state which is $4 \times 9 = 6^2$, but the orbital development is 20 from M_2 to M_3 . Similarly, at the energy space development up to E_5 , the distinguishable matter development would be represented by the state M_4 total M up to which is $4 \times 16 = 8^2$ and the orbital development is $7 \times 4 = 28$ from M_3 state to M_4 state.

Instead of taking the energy squares as in fig. 46 if only progressive development of distinguishable phases of matter development from a previous matter state to next in sequence would be considered, the progressive development of matter phases could be condensed into fig. 48 in the square continuum. The purpose is to show the development of distinguishable matter phases in sequence from previous to next and to show the results therefrom to be in conformity with the progressive development of electron in distinguishable atoms in the order of increasing magnitudes of atomic matter intensity (say atomic number).

In the previous works it has been shown that the atomic numbers in the conventional periodic classification of elements differ from the present theory less by 2. The conventional number of elements in the various periods are less than those in the present theory by 2.

Conventional: 2, 8+8, 18+18, 32+32.....

In the present theory the number of distinguishable chemical elements in the various periods are:

2+2, 8+8, 18+18, 32+32

The suggestion has been put forward to make up the first group of 4 elements by ortho-hydrogen, neutron, para-hydrogen and helium.

From fig. 48, the progressive development of electron in the elements would be given by the following:

At the M_1 state this should be 4 or $2+2$. At the M_2 state while the total number is 16 or $8+8$,

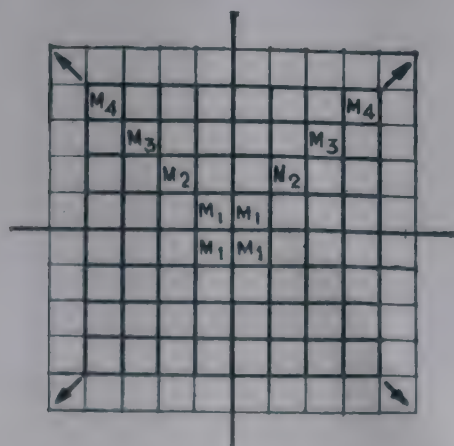


Fig. 48

the orbital development from the previous M_1 state towards M_2 state would be from $2+2$, for M_1 state to $6+6$ to M_2 state. This would be borne out by the development of electrons in the orbits of $\text{Li} \rightarrow \text{Fl}$ towards Ne and $\text{Na} \rightarrow \text{Cl}$ towards A in the periodic series.

The distinguishable matter development in the periodic series at the M_3 state are 36 in total and the orbital development is 20, i.e. $10+10$. This will be borne out by 4th and 5th series of elements in the periodic table in which the additional numbers corresponding to M_2 state is 10 which are the number of transitional elements in 4th and 5th series from K to Kr and Rb to Xe respectively. In the next matter state M_4 , the total number of distinguishable matter generated would be 64 and orbital development from the previous M_3 state to the new M_4 state would be 28, i.e. $14+14$. Addition of 14 number of electrons in the orbit or 14 number of atomic elements in the 7th series would be borne out by the addition of 14 rare earth group elements from the previous M_3 state.

Though from the 4 directional square development in plane the matter development in terms of squares in sequence is represented by $2^2, 4^2, 6^2$ which is same as 4 [$1^2, 2^2, 3^2, 4^2 \dots$] the linear developments in 4 directions can be expressed as

$$4 [(\sqrt{1})^4, (\sqrt{2})^4, (\sqrt{3})^4, (\sqrt{4})^4 \dots]$$

Algebraically matter development can be expressed as $4 [(\sqrt{(a-1)})^4]$ in which 'a' can have any value as 1, 2, 3, 4.....

The algebraical formula corresponding to total energy matter space development would be $[(\sqrt{(a+1)})^4]$ in which a can have only even values as 0, 2, 4.... and the progressive orbital development of the matter phases can be expressed as $\sqrt{(a+1)^4} - \sqrt{(a-1)^4}$ in which 'a' is odd or by the formula $\sqrt{(a+2)^4} - \sqrt{(a-0)^4}$ where 'a' is even.

Fig. 48 would further clarify that the series $0^2, 2^2, 4^2, 6^2 \dots$ incorporates neither total matter energy evolution nor $2a/(a+1)^2$ portion of energy matter phase in the universal evolutionary wave of energy matter manifestation.

If this Universal Law were understood in proper perspective deficiencies of energy matter equivalence as well as those quantum theory would have been revealed. In fact, many aspects of quantum theory approach move closely towards the present approach, but application of Einstein's theory is confronted with more than one alternative interpretation.

Since $E/M=C^2$ can be interpreted to apply to $\frac{a^2}{(a+1)^2}$

which could conform to only condensed phase in the wave continuum. It could also be interpreted to only $\frac{2a}{(a+1)^2}$ relative to vapour phase.

But $E/M=C^2$ would not apply to both simultaneously taken together, for which a fundamental law is sought for to cover all aspects of energy matter relationship which are involved in energy matter manifestation.

(8) Condensation—Vaporisation, Fusion—Fission

This involves important questions about the nature of equilibrium existence of elementary matter and their stability independently or in association as are found in the earth's atmosphere and their distribution on the surface of earth in the universal context. Why the lighter gaseous elements are found to occur in associated form as multi-atomic molecules? As the atomic weights of such elementary gases increase, the tendency is towards their equilibrium existence as in their mono-atomic state. In the other extreme case why the atoms of highest matter intensity only undergo radio-active disintegration on the surface of the earth? And why there are elements in between these extreme groups which are stable and which exist in their mono-atomic state on earth?

The answers to these questions would be available from perusal of the postulates in the present theory. According to this theory the lightest element hydrogen (atomic) should have its natural equilibrium space association in which the photon of space would be of highest energy as well as matter intensity. The heaviest atom in the universal context should have its natural associated equilibrium space in which the photon of space should have least energy as well as matter intensity.

In these explanations atomic matter and photonic space should be understood in proper perspective. Atom and the surrounding equilibrium space are two phases in equilibrium: atomic state is like condensed phase as liquid and surrounding space of so called photons is like vapour phase. Significance of matter intensity of atom is clear. Significance of matter intensity of photons of space means that at different energy intensity of surrounding space in equilibrium with atoms of varying matter and energy intensity the space constituent photon will have varying matter intensity too, just as H_2O in vapour phase at different temperatures has different vapour densities and tension while in equilibrium with liquid phase.

While analysing the two phenomena of atomic fission and fusion, the twin phase aspects in the reaction which are involved should be distinguished. The process of Li when it is brought to a higher energised state of He after reaction with proton is similar to the phenomenon of heating a liquid to a higher temperature, say critical state; from that state relative to ground state of lower temperature there will be certain release of energy. Compared to this Hydrogen and Oxygen when combine to form super heated H_2O and brought to critical state with respect to the same ground state there will be energy release. The available energy in the latter case is much greater than the former. Available energy in case of fusion is similar to the latter case and available energy in fission is similar to that obtainable in former case. $^2D+^2D=^4He$ reaction is comparable to the latter case. The difference in energy availability in the two cases is obvious.

The above explanation was necessary because in our conventional understanding in the two types of reactions, which reactants are in which phase and whether above or below a relevant critical state is not clear. Once these aspects are clear significance of the two processes will not be difficult to reconcile in the light of the present theory. Suppose the element hydrogen with its atomic configuration, due to some reason suddenly finds itself in an atmosphere of associated space in which the photon of space has less matter and energy intensity than its natural equilibrium space with which the element would have been generated in equilibrium. The present theory demands that in the new environment the equilibrium matter intensity of hydrogen atom in such an associated space of less energy and matter intensity, the atomic matter intensity of hydrogen should have higher value. It can be construed that this condition would be satisfied if in such environment two or more hydrogen atoms are combined to produce an aggregate of more atoms than one per position; thus the matter intensity of hydrogen per position increases and in that state it can remain in equilibrium with its new space surrounding. Thus on the Sun's surface hydrogen could be mono-atomic and in earth's atmosphere it could be diatomic.

Take the other extreme case. An elementary matter atom of high matter intensity like Uranium which should have its natural associated equilibrium space of photon having low matter as well as low energy intensity relative to that of hydrogen. If such an element is brought to a new situation in which the Uranium atom has an associated surrounding space which has photon of space having higher energy as well as matter

intensity than its natural equilibrium with Uranium, then as per the present theory, in this new situation, the atom of Uranium should be converted into an atom having less matter intensity in conformity with what should be in equilibrium with the new surrounding space. This would therefore mean that the original Uranium atom, must undergo disintegration to suit the new conditions by being itself converted into lighter atoms.

The behaviour of atoms in the above illustration is similar to the observed behaviour of constituents of vapour and liquid phases in equilibrium. If a liquid near about its gas/liquid critical point suddenly finds itself situated in a vapour atmosphere state where vapour density and temperature is less than its natural equili-

brium vapour state near to the gas/liquid critical state, the liquid phase will be cooled down and its intensity will be increased. This is similar in significance to converging of two or more atoms per position to form an aggregate leading to higher matter intensity per position in the new equilibrium state. Again, if a liquid at a very low temperature with its natural low equilibrium vapour density and temperature suddenly finds itself in an atmosphere of higher vapour density and higher temperature, corresponding say, near about the gas/liquid critical state, the liquid would expand by disintegration undergoing phenomenon similar to the disintegration of Uranium atom in similar circumstances, in order for the liquid phase to attain a lower density or lower matter intensity and higher vapour density.

